Harbor Communities Monitoring Study (HCMS) Saturation Monitoring of Toxic Air Contaminants and Related Pollutants

Eric M. Fujita, J. Brooks Mason,
David E.Campbell and Barbara Zielinska

Division of Atmospheric Sciences
Desert Research Institute
Nevada System of Higher Education
Reno, Nevada

Sacramento, CA
April 26, 2010

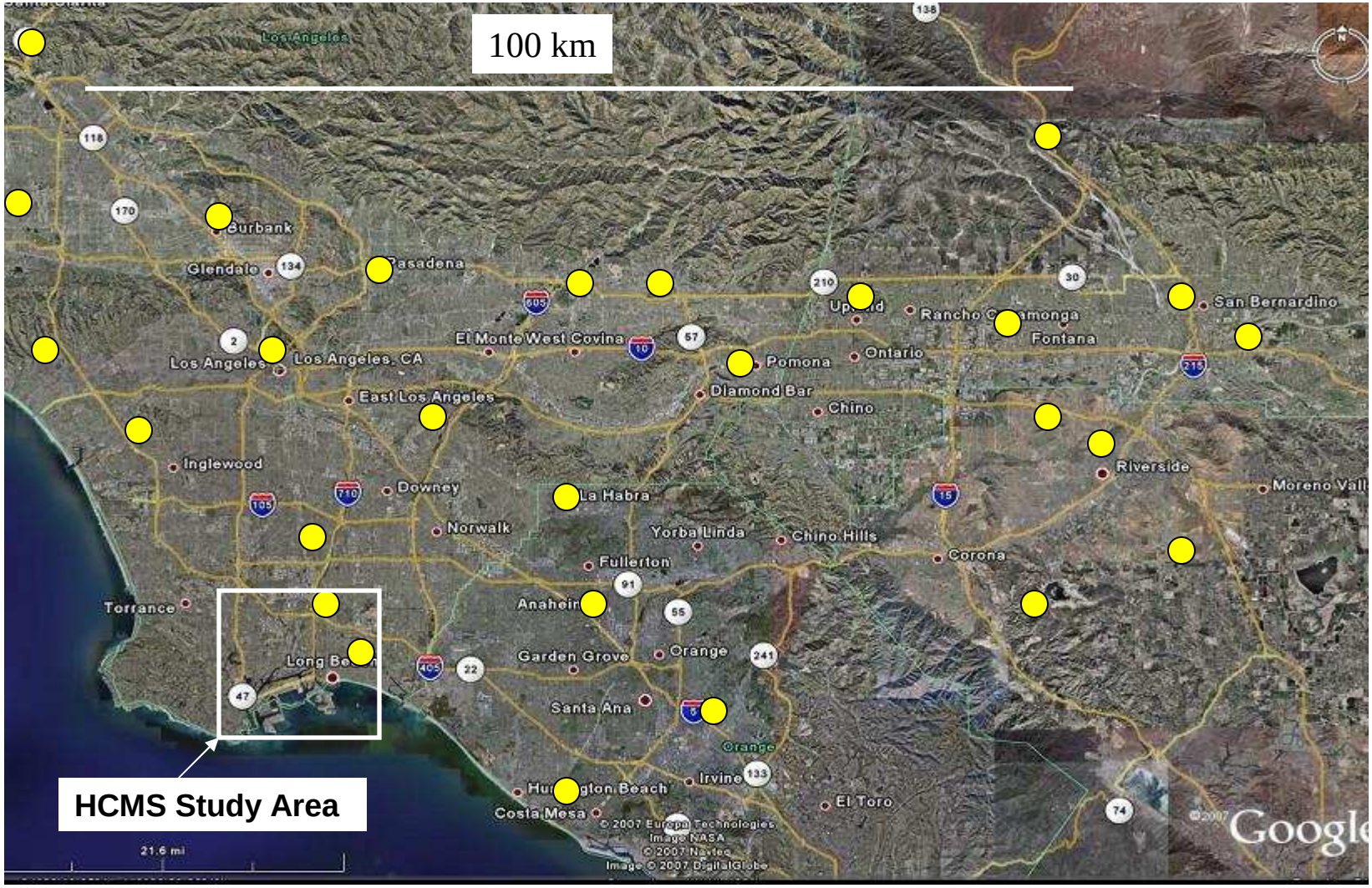
Acknowledgments

- **Sponsors**
  - California Air Resources Board
  - South Coast Air Quality Management District
- **Support**
  - DRI Organic Analytical Laboratory: Barbara Zielinska, Brooks Mason, Mark McDaniel and Anna Cunningham
  - DRI Environmental Analysis Facility: Judith Chow, Steven Kohl, Brenda Cristani and Dana Trimble

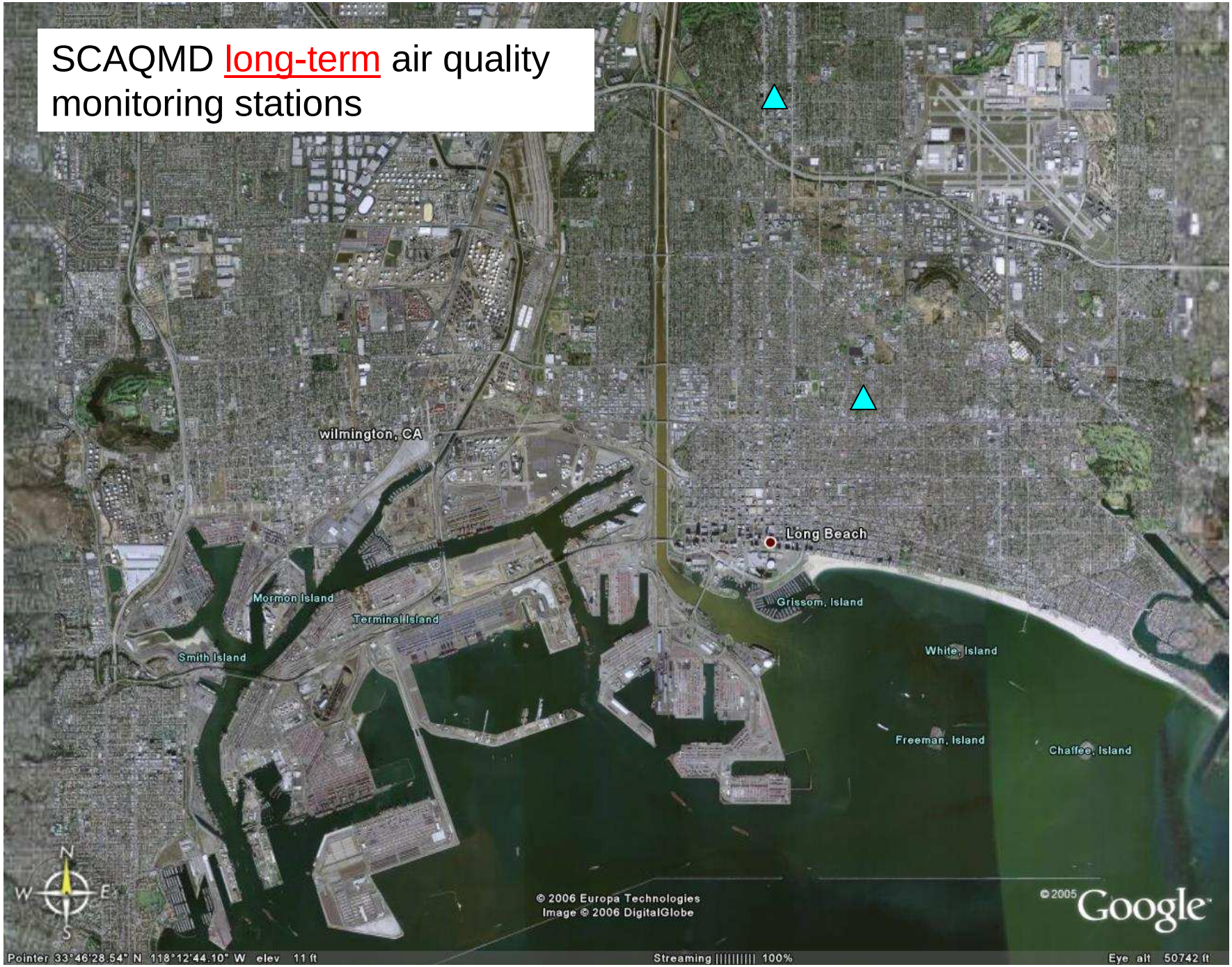
Overview of Presentation

- Saturation monitoring objective.
- Passive monitoring methods. Laboratory and field evaluations.
- Saturation monitoring network design.
- HCMS saturation monitoring results.
- Comparisons of HCMS and MATES-III data and results from recent on-road and near-road studies.

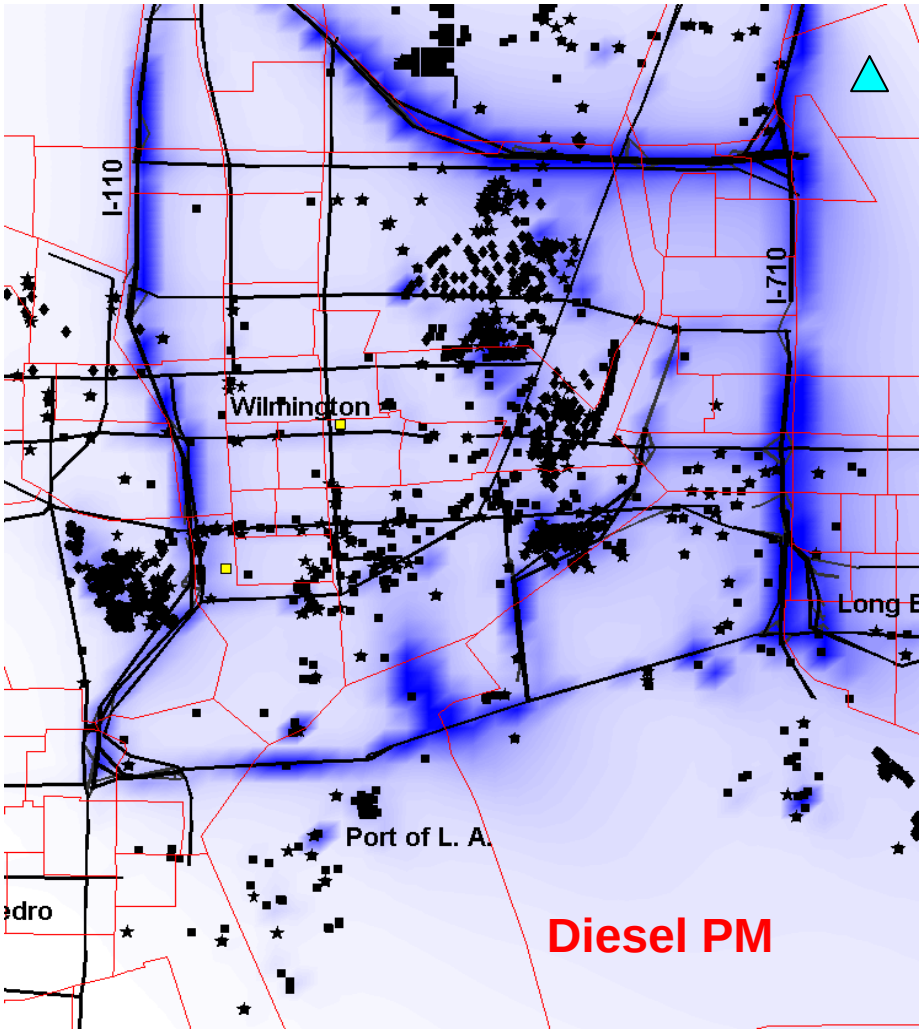
SoCAB Air Monitoring Stations

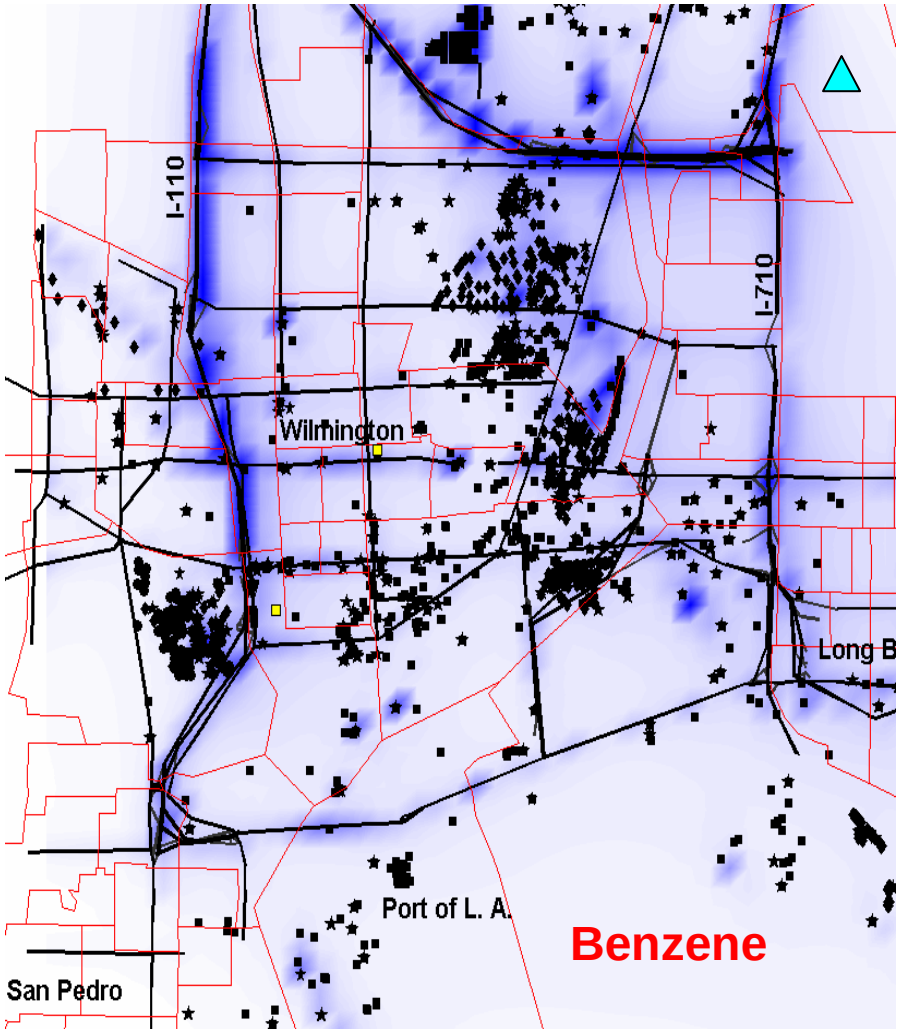


SCAQMD long-term air quality monitoring stations



Spatial Variations in Pollutant Concentrations in Wilmington from Modeled Estimates





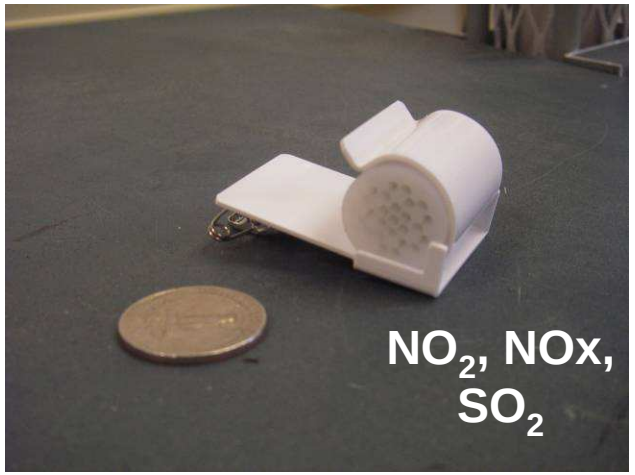
Source: CARB, Air Toxics Assessment in Wilmington, CA, (Project Status Update), August 12, 2004.

HCMS Saturation Monitoring Hypotheses

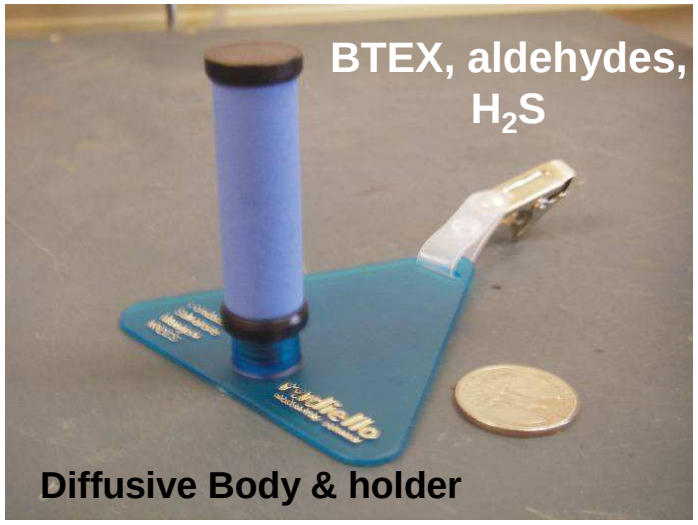
1. Passive monitoring methods have sensitivity and precision comparable to conventional monitoring methods (averaged over the same period).
2. Gradients in pollutant concentrations exist within the Harbor Communities and can be related to a location's proximity to emissions from either stationary or mobile sources.
3. The long-term air quality monitoring in the area is not adequate to characterize the spatial variations in cumulative exposure within the community.

Sampling Methods

AirMetric Minivol Aerosol Sampler



Ogawa passive samplers



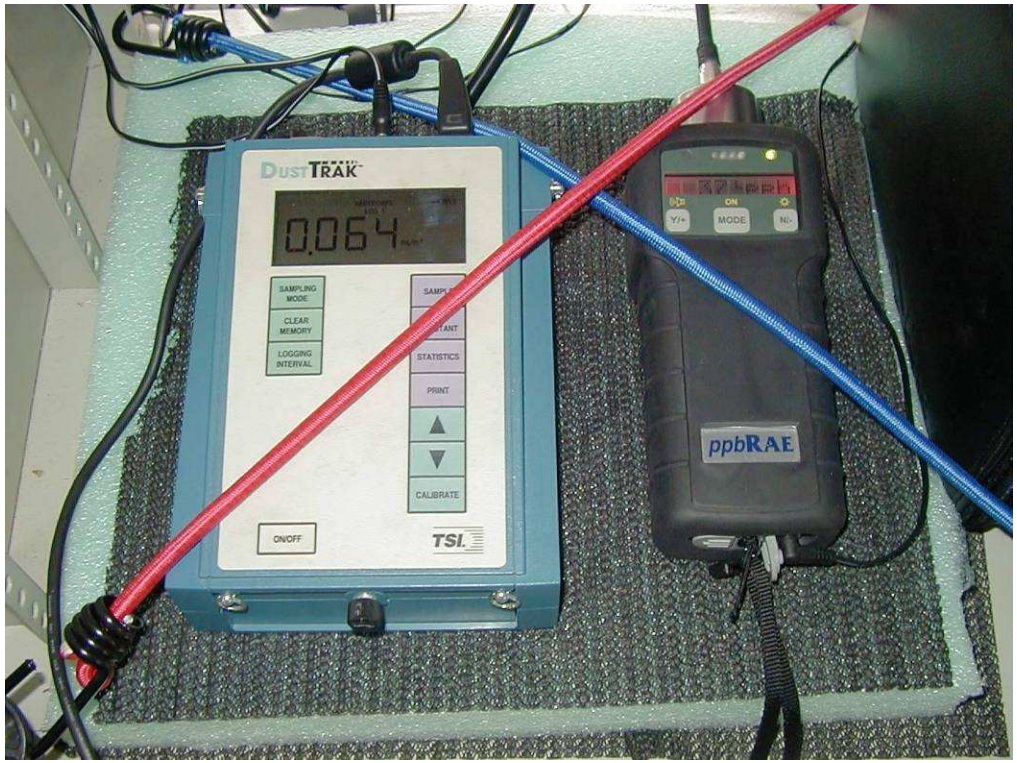
Diffusive Body & holder

Adsorbent tubes

Radiello passive samplers

Continuous Instruments

DRI Photoacoustic
black carbon



TSI DustTrak
$PM_{2.5}$ Mass

RAE System ppbRAE
Portable Photoionization Detector
VOC

Overview of Presentation

- Saturation monitoring objective.
- **Passive monitoring methods. Laboratory and field evaluations.**
- Saturation monitoring network design.
- HCMS saturation monitoring results.
- Comparisons of HCMS and MATES-III data and results from recent on-road and near-road studies.

How Diffusive Samplers Work

Theoretical basis is Fick's First Law of Diffusion

$$J = -D\frac{\partial C}{\partial x}$$

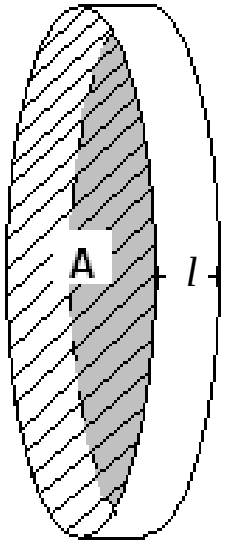
where

- $J = m/At$, diffusion flux (mass length^{-2} time^{-1})
- D = diffusion coefficient (length^{2} time^{-1})
- C = concentration (mass length^{-3})
- x = distance (length)

Sampling Rate of Diffusive Samplers

$$\frac{dm}{dt} = DA\frac{dC}{dl}$$

$$\frac{m}{t} = D\frac{A}{l}(C - C_o)$$



If C at absorbing surface (C_o) is negligible, equation can be approximated to

$$\frac{m}{tC} = D\frac{A}{l} = Q$$

Q = sampling rate (l/min)

$$C = \frac{m}{tQ}$$

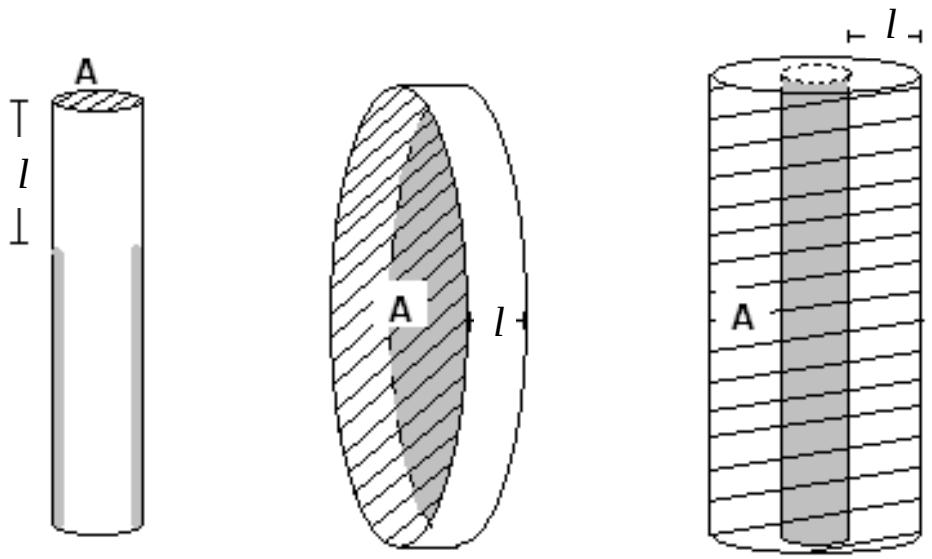
C is determined from mass of analyte trapped on the absorbent and time of exposure, t

Sampler Geometry

$$\frac{m}{tC} = D\frac{A}{l} = Q$$

To improve analytical sensitivity m should be increased by increasing Q.

Since D is constant, Q is proportional to A/l.



Tube Shield Radial

Increasing Q →

l = path length; A = diffusive path area (dashed area)
Grey area represents adsorbent surface

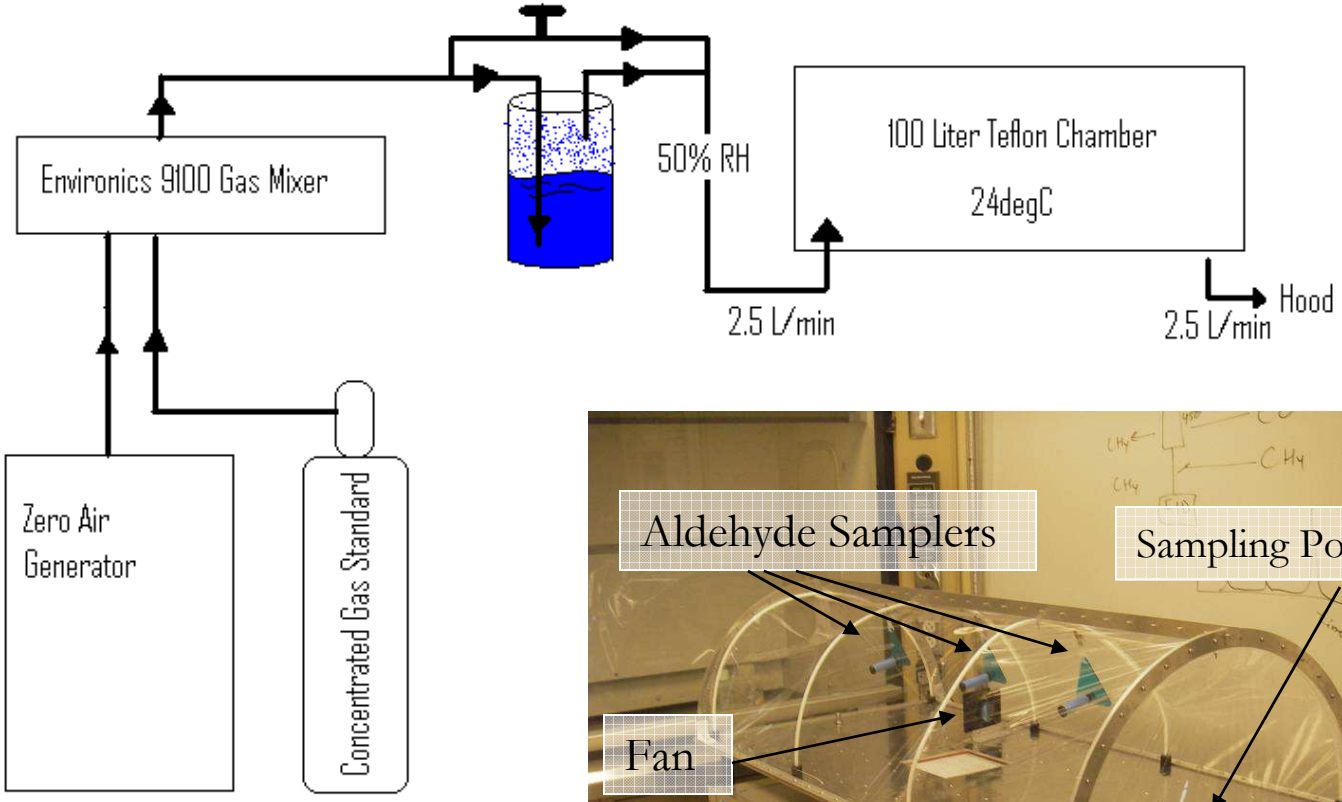
HCMS Passive Sampling

Pollutant	Diffusive Body	Adsorbent	Analytical Method	MDL (ppbv) (168 hours exposure)
NO_2	Ogawa 3300	Triethanolamine	Colorimetry for nitrite	**0.32**
NOx		Triethanolamine + PTIO	Colorimetry for nitrite	**0.32**
SO_2		Triethanolamine	Ion Chromatography for sulfate	**0.54**
H_2S	Radiello 120-1	zinc acetate	Visible spectrometry	**0.14**
VOC	Radiello 120-2	graphitic charcoal (Carbograph 4)	Thermal Desorption GC/MS	**benzene 0.015** **etbenzene 0.022** **toluene 0.002** **xylenes 0.002**
Carbonyl Compounds	Radiello 120-1	DNPH coated florisil	HPLC-UV	**formaldehyde 0.07** **acetaldehyde 0.05** **acrolein 0.12**

Evaluation of Passive Sampling Methods Used in the HCMS

- **Laboratory evaluations**
  - Precision, accuracy, and sampling rates evaluated using flow-through chamber with known pollutant concentration.
- **Pilot study**
  - Determine replicate precision under field conditions.
  - Compare passive methods with continuous instruments and active sampling methods.
- **Quality assurance during main study**
  - Triplicate sampling at one site collocated with existing SCAQMD air quality monitoring station.
  - Passive sampling compared to active sampling by DRI and SCAQMD continuous instruments.

Chamber Experiment Setup



Chamber Experiments

Sampler Type	Analyte	Nominal Concentration	Reference Method
Ogawa NO_2	NO_2	25 ppb	Horiba NO/NOx Analyzer
Ogawa NO_x	NO_x	54 ppb	Horiba NO/NOx Analyzer
Radiello Aldehyde	Formaldehyde	5 ppb	Waters DNPH by HPLC
Radiello VOC	BTEX	1.5 ppb	Canister GC/MS
Radiello H_2S	H_2S	2 ppb	N/A

- Exposure times - 1, 4 and 7 days.
- Storage of 7 day exposure samples – 1, 7, 14 days before analysis.
- Nominal concentrations are dilutions of standards to expected ambient averages.
- Reference method used to evaluate diffusion rate.

Chamber Experiment Results

Compounds	n	Passive Sample (ppbv) [1]	Passive RSD (%)	Reference Value (ppbv) [2]	Passive-Ref % Δ [3]
NO_x	3	39.8 ± 0.6	1.6%	39.00	2%
NO_2	3	21.5 ± 0.3	1.4%	21.80	-1%
Formaldehyde	3	5.08 ± 0.36	2.0%	5.20	-2%
H_2S	3	1.99 ± 0.04	2.0%	2.10	-5%
Benzene	3	2.10 ± 0.24	4.9%	2.57	-18% or (1%) [4]
Toluene	3	2.24 ± 0.11	6.7%	2.37	-5%
Ethylbenzene	3	1.80 ± 0.12	4.5%	1.28	41% or (-6%) [4]
m,p-Xylene	3	0.89 ± 0.04	5.3%	1.02	-13%
o-Xylene	3	0.38 ± 0.02	7.1%	0.43	-12%

[1] Mean value ± standard deviation

[2] Reference method is by Horiba NO/ NOx analyzer, 24-hour canisters for BTEX, and dilution of standards for formaldehyde and H_2S

[3] Percent difference of passive minus reference results.

[4] Using our experimentally determined sampling rates of 22.4 and 37.4 ml/min (in parenthesis) rather than 27.8 and 25.7 ml/min published by Radiello for benzene and ethylbenzene respectively.

HCMS Pilot Study – Field Evaluation

- Study Site
  - North Long Beach AQMD Station
  - August 2006

- Objectives
  - Evaluate replicate precision and accuracy of passive samplers under field conditions.
  - Evaluate effect of stagnant nighttime air on sampling rate.

Pilot Study Results

Compounds	n	Ambient Winds (ppbv) [1]	Fan-Induced Winds (ppbv) [1]	Passive RSD (%)	Reference Value (ppbv) [2]	Amb-Fan % Δ [3]	Amb-Ref % Δ [4]
NO_x	3	22.3 ± 0.8	22.9 ± 0.6	2.2%	28.0	-3%	-20%
NO_2	3	14.1 ± 0.5	14.4 ± 1.2	5.9%	17.2	-2%	-18%
SO_2	3	1.4 ± 0.2	1.2 ± 0.2	15.5%	1.7	16%	-18%
Formaldehyde	3	1.23 ± 0.04	1.27 ± 0.12	6.4%	1.10	-3%	12%
Acetaldehyde	3	0.59 ± 0.01	0.59 ± 0.03	3.4%	1.04	<1%	-43%
H_2S	3	0.31 ± 0.15	0.26 ± 0.08	39.6%		18%	
Benzene	3	0.29 ± 0.03	0.29 ± 0.01	6.9%	0.37	<1%	-22% or (-3%) [5]
Toluene	3	1.31 ± 0.22	1.19 ± 0.17	15.5%	1.09	10%	20%
Ethylbenzene	3	0.17 ± 0.01	0.18 ± 0.01	5.7%	0.13	-6%	31% or (-8%) [5]
m,p-Xylene	3	0.46 ± 0.04	0.49 ± 0.01	5.4%	0.45	-6%	2%
o-Xylene	3	0.18 ± 0.01	0.20 ± 0.01	5.3%	0.18	-11%	<1%

[1] Mean value ± standard deviation

[2] Reference are NO/NOx and SO_2 analyzers and DRI canisters and DNPH cartridges.

[3] Percent difference of results for ambient and fan-induced winds.

[4] Percent difference of the passive result (without fan) compared to the reference result.

[5] Using our experimentally determined sampling rates of 22.4 and 37.4 ml/min (in parenthesis) rather than 27.8 and 25.7 ml/min published by Radiello for benzene and ethylbenzene respectively.

Average Mixing Ratios of Passive Measurements at the Hudson Monitoring Station and Replicate Precision

	DQO [1]		HCMS Winter			HCMS Summer		
	MDL	Precision	Mean	Precision [2]		Mean	Precision [2]	
	ppbv	%	ppbv	ppbv	%	ppbv	ppbv	%
Nitrogen Oxides (NOx)	0.32		73.0	2.03	2.8%	29.4	0.65	2.2%
Nitorgen Dioxide (NO_2)	0.32		28.5	1.50	5.3%	19.5	0.96	4.9%
Sulfur Dioxide (SO_2)	0.54		1.1	0.107	9.8%	1.0	0.196	19.8%
Hydrogen Sulfide (H_2S)	0.20	8.7%	0.8	0.036	4.8%	0.9	0.117	12.5%
Benzene	0.015	8.3%	0.6	0.014	2.3%	0.3	0.026	7.5%
Toluene	0.002	8.3%	1.7	0.039	2.3%	1.0	0.044	4.2%
Ethylbenzene	0.002	9.1%	0.3	0.008	2.4%	0.2	0.014	6.7%
Xylenes	0.002	11.3%	1.4	0.031	2.2%	0.7	0.063	9.2%
Formaldehyde	0.07	13.8%	2.7	0.06	2.2%	1.8	0.12	6.7%
Acetaldehyde	0.05	15.9%	1.9	0.05	2.8%	0.7	0.03	4.7%
Acrolein	0.120	16.5%	0.028	0.015	52.0%	0.010	0.005	47.4%

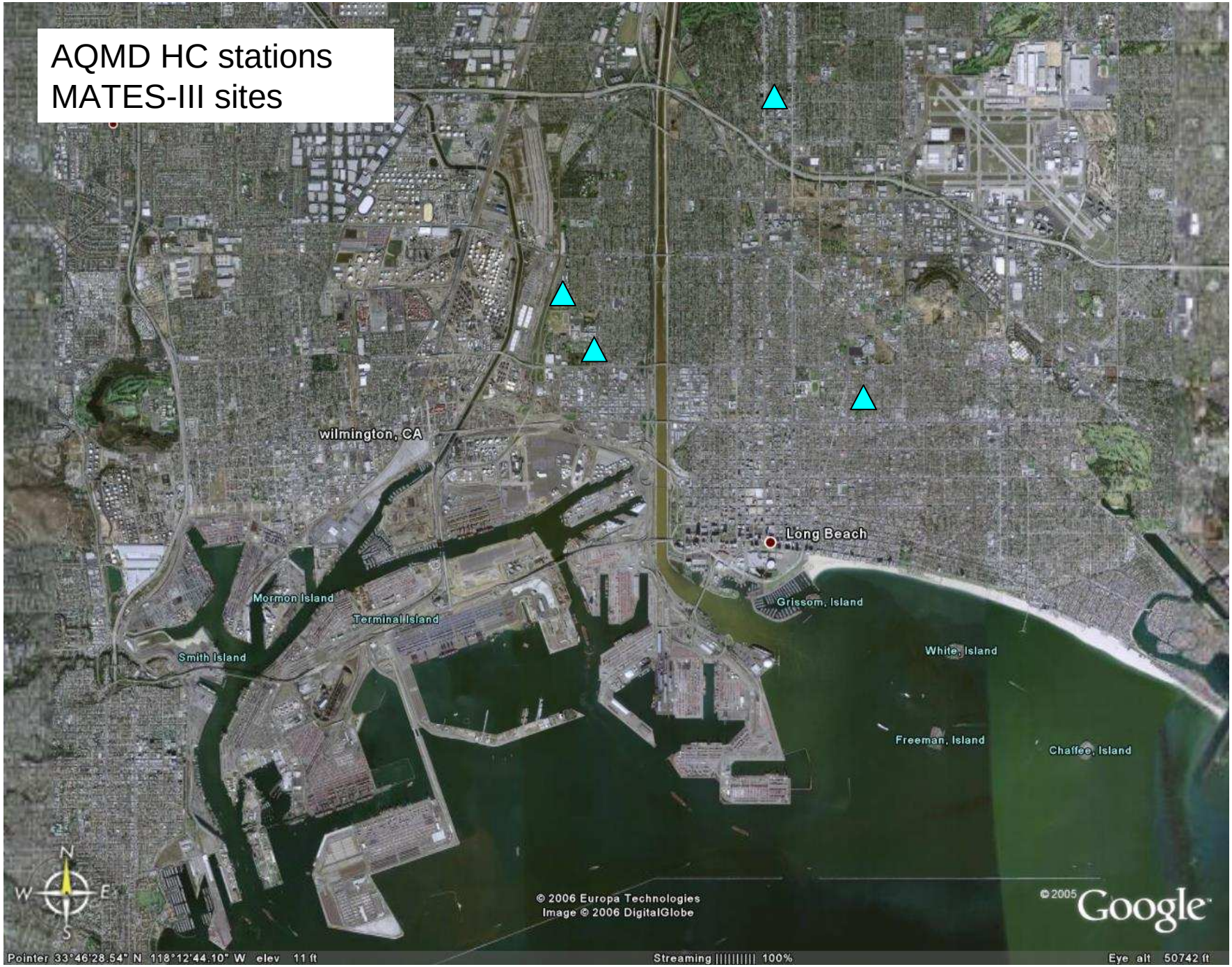
1 Data quality objectives (DQO) are manufacturers' specifications for 7-day exposures and one σ precision.

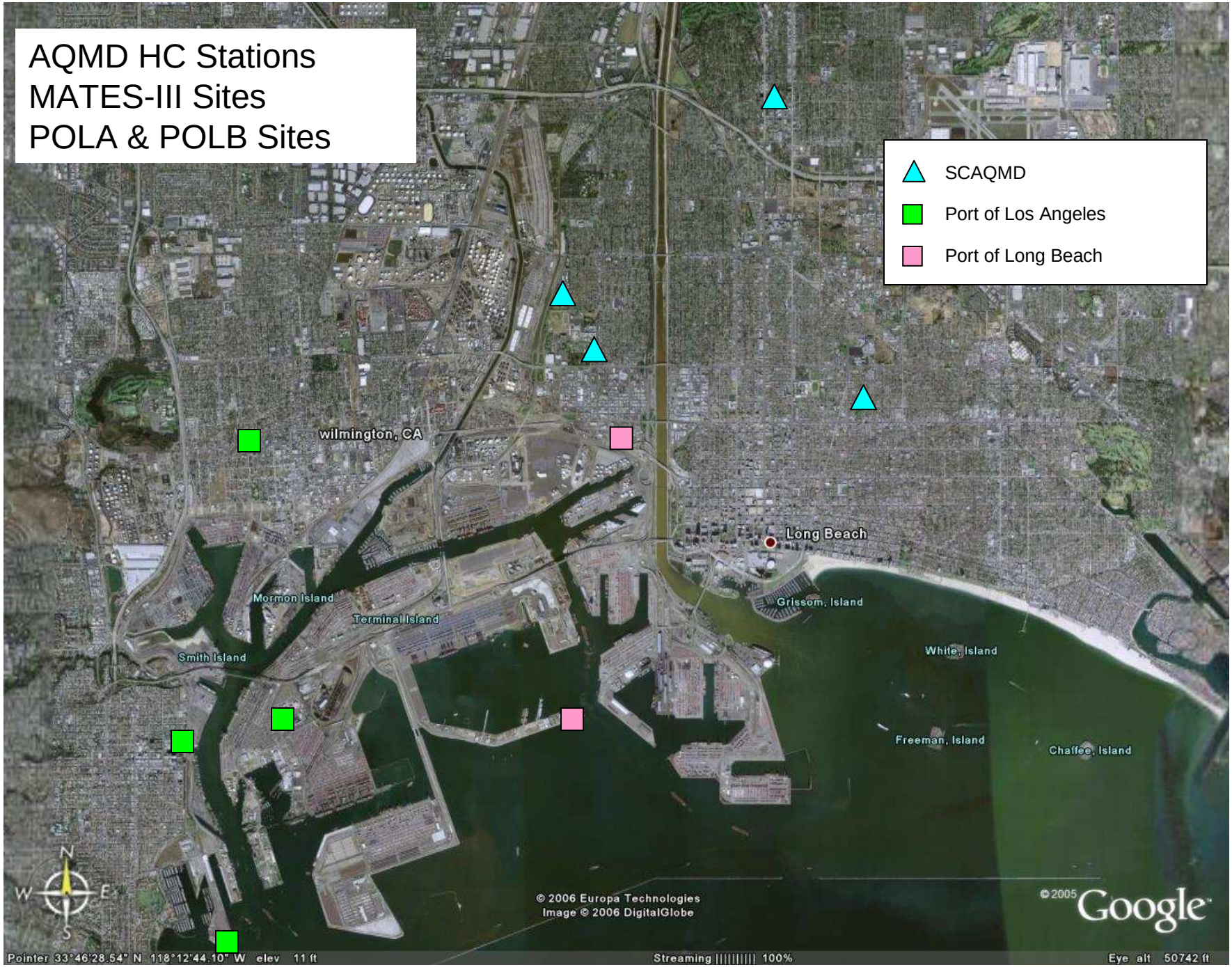
2 Mean of the absolute differences between average of triplicates and individual sample (12 values per season).

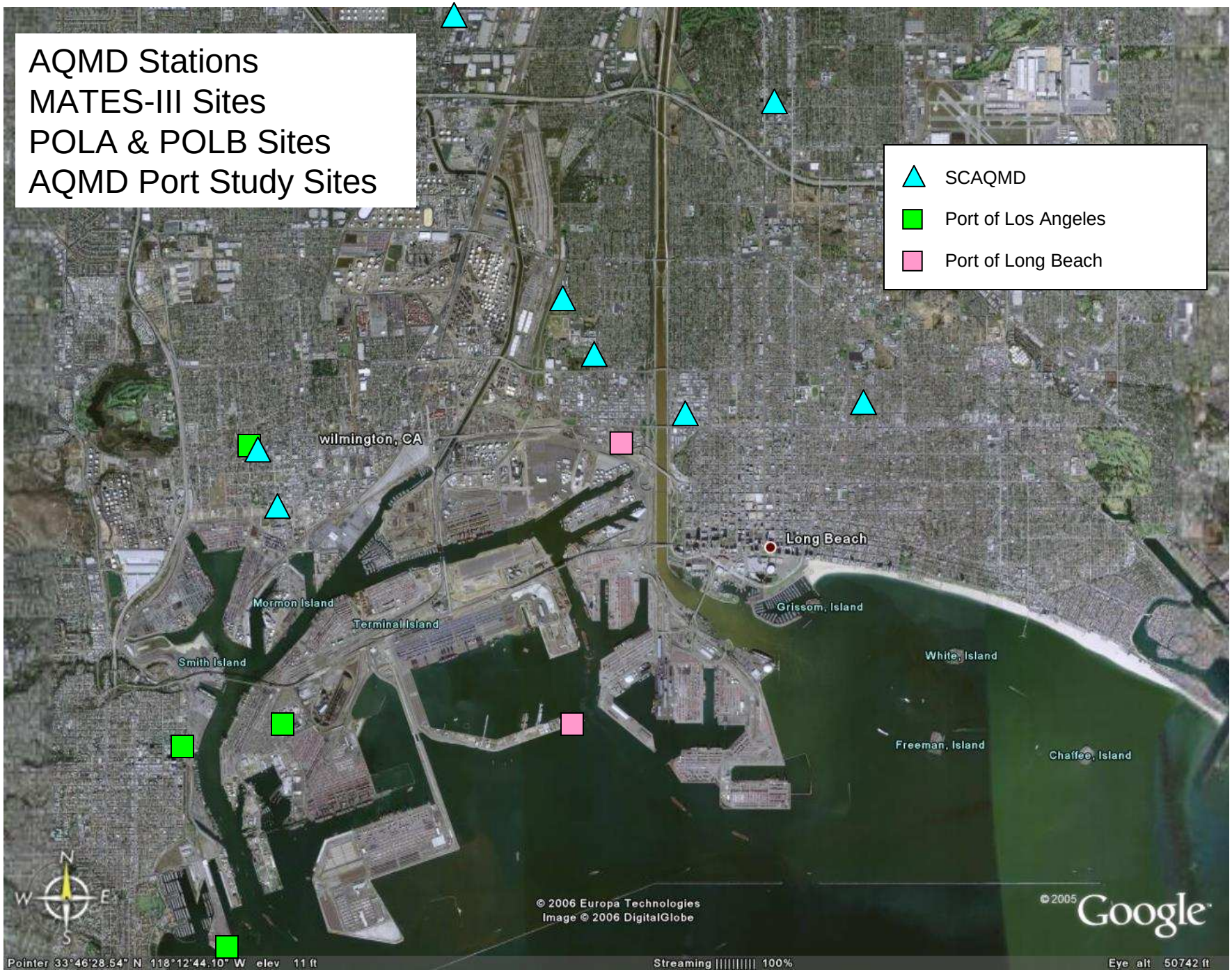
Note: Shaded values denote mean ambient values that are less than five times the minimum detection limit (MDL).

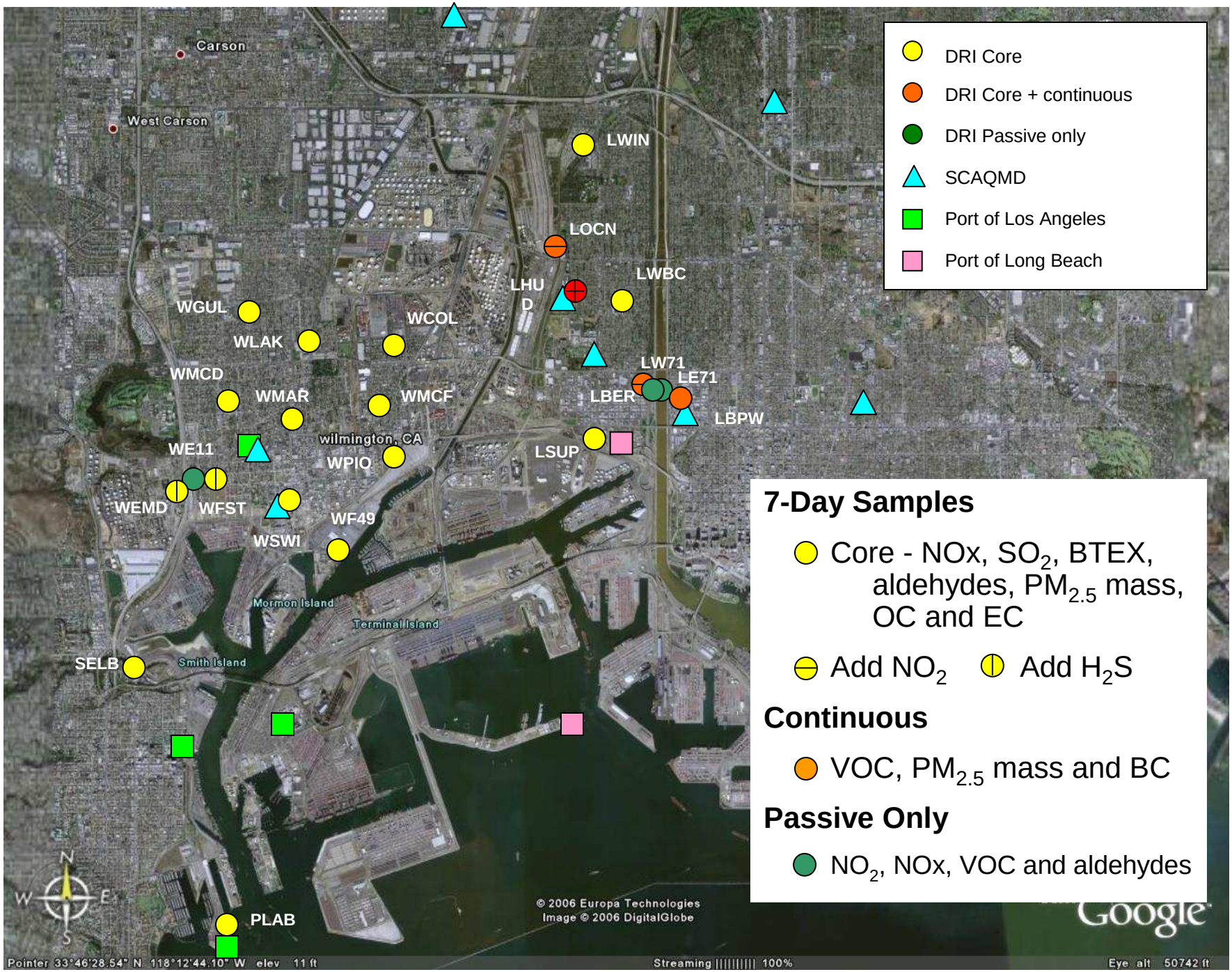
Overview of Presentation

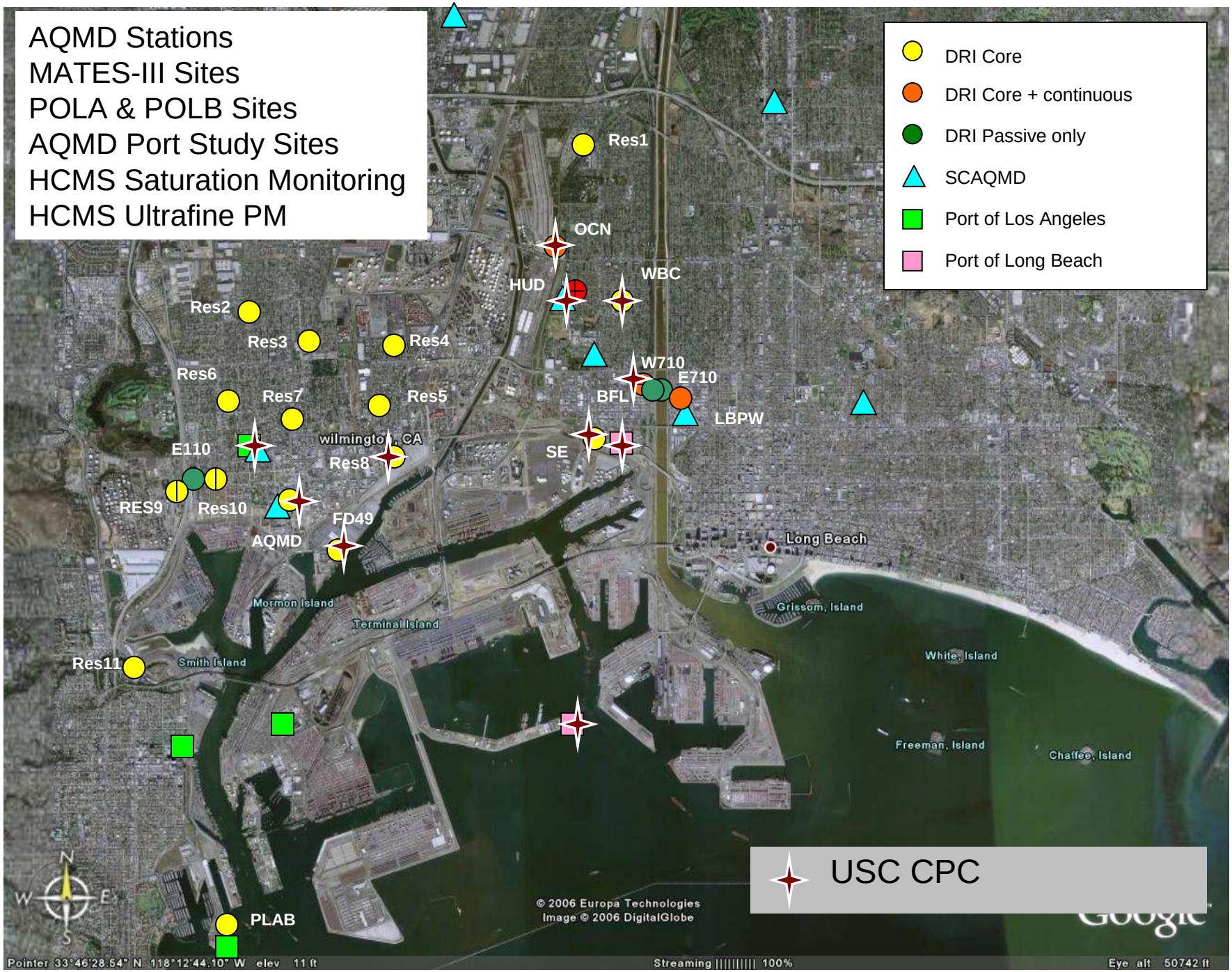
- Saturation monitoring objective.
- Passive monitoring methods. Laboratory and field evaluations.
- **Saturation monitoring network design.**
- HCMS saturation monitoring results.
- Comparisons of HCMS and MATES-III data and results from recent on-road and near-road studies.


AQMD HC stations
MATES-III sites
wilmington, CA
Long Beach
Mormon Island
Terminal Island
Smith Island
Grissom, Island
White, Island
Freeman, Island
Chaffee, Island
© 2006 Europa Technologies
Image © 2006 DigitalGlobe
© 2005 Google
Pointer 33°46'28.54" N 118°12'44.10" W elev 11 ft
Streaming 100%
Eye alt 50742 ft

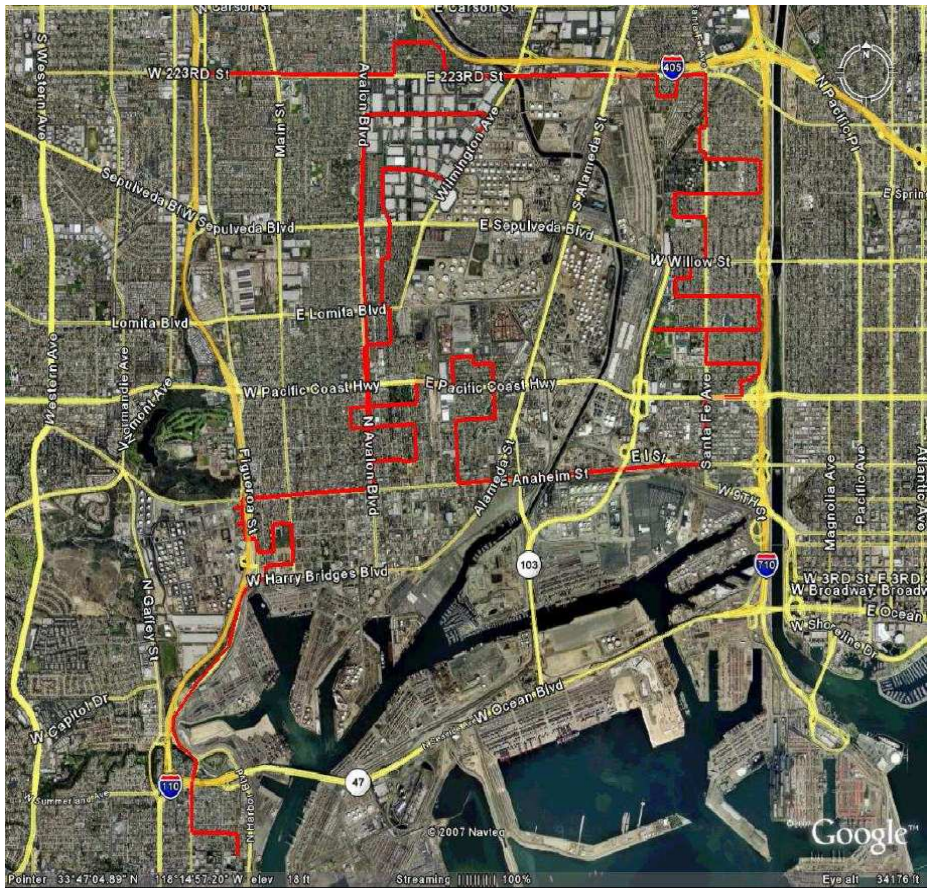

AQMD HC Stations
MATES-III Sites
POLA & POLB Sites
SCAQMD
Port of Los Angeles
Port of Long Beach
wilmington, CA
Long Beach
Mormon Island
Terminal Island
Smith Island
Grissom, Island
White, Island
Freeman, Island
Chaffee, Island
© 2006 Europa Technologies
Image © 2006 DigitalGlobe
©2005 Google
Pointer 33°46'28.54" N 118°12'44.10" W elev 11 ft
Streaming 100%
Eye alt 50742 ft

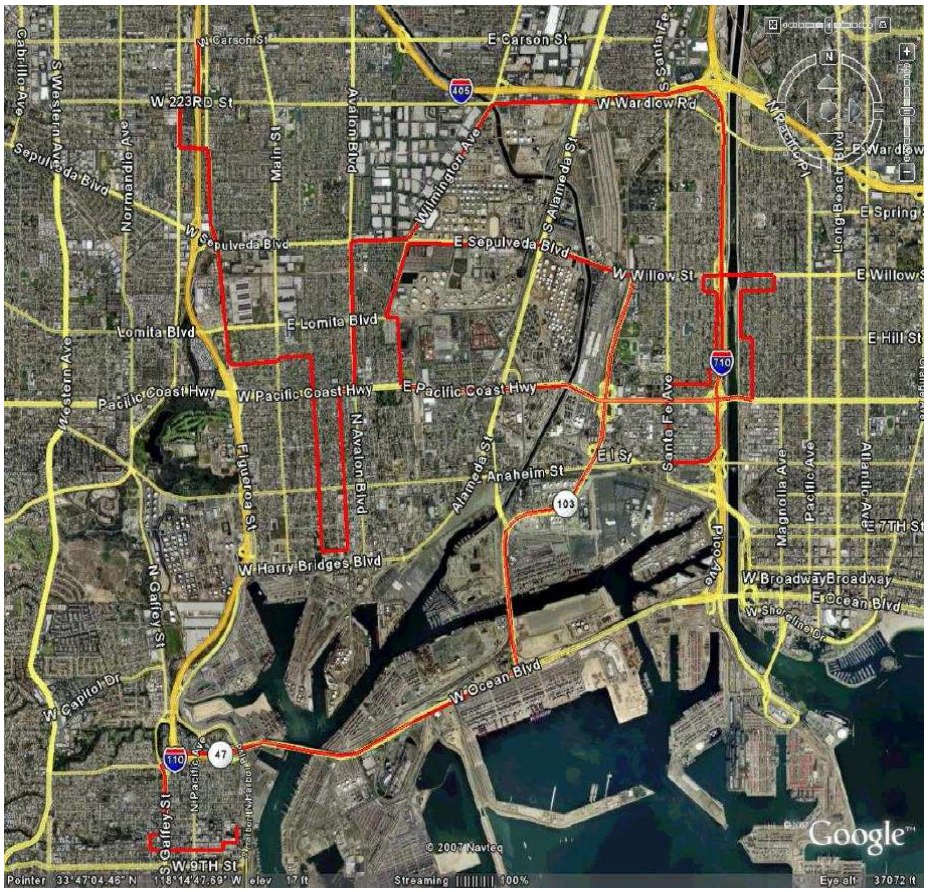

AQMD Stations
MATES-III Sites
POLA & POLB Sites
AQMD Port Study Sites
SCAQMD
Port of Los Angeles
Port of Long Beach
wilmington, CA
Long Beach
Mormon Island
Terminal Island
Smith Island
Grissom, Island
White, Island
Freeman, Island
Chaffee, Island
© 2006 Europa Technologies
Image © 2006 DigitalGlobe
©2005 Google
Pointer 33°46'28.54" N 118°12'44.10" W elev 11 ft
Streaming 100%
Eye alt 50742 ft


Carson
West Carson
LWIN
LOCN
LHU
D
LWBC
WGUL
WCOL
WLAK
WMCD
WMAR
WMCF
LW71
LE71
LBER
LBPW
wilmington, CA
WE11
WPIO
LSUP
WEMD
WFST
WF49
WSWI
Mormon Island
Terminal Island
SELB
Smith Island
PLAB
DRI Core
DRI Core + continuous
DRI Passive only
SCAQMD
Port of Los Angeles
Port of Long Beach
7-Day Samples
Core - NOx, SO2, BTEX, aldehydes, PM2.5 mass, OC and EC
Add NO2
Add H2S
Continuous
VOC, PM2.5 mass and BC
Passive Only
NO2, NOx, VOC and aldehydes
© 2006 Europa Technologies
Image © 2006 DigitalGlobe
Google
Pointer 33°46'28.54" N 118°12'44.10" W elev 11 ft
Streaming 100%
Eye alt 50742 ft


AQMD Stations
MATES-III Sites
POLA & POLB Sites
AQMD Port Study Sites
HCMS Saturation Monitoring
HCMS Ultrafine PM
DRI Core
DRI Core + continuous
DRI Passive only
SCAQMD
Port of Los Angeles
Port of Long Beach
USC CPC
Res1
OCN
HUD
WBC
Res2
Res3
Res4
Res6
Res7
Res5
W710
E710
BFL
LBPW
E110
Res8
SE
RES9
Res10
FD49
AQMD
Long Beach
Mormon Island
Terminal Island
Grissom, Island
White, Island
Res11
Smith Island
Freeman, Island
Chaffee, Island
PLAB
© 2006 Europa Technologies
Image © 2006 DigitalGlobe
Google
Pointer 33°46'28.54" N 118°12'44.10" W elev 11 ft
Streaming 100%
Eye alt 50742 ft

Harbor Communities Monitoring Study
Mobile Sampling Routes



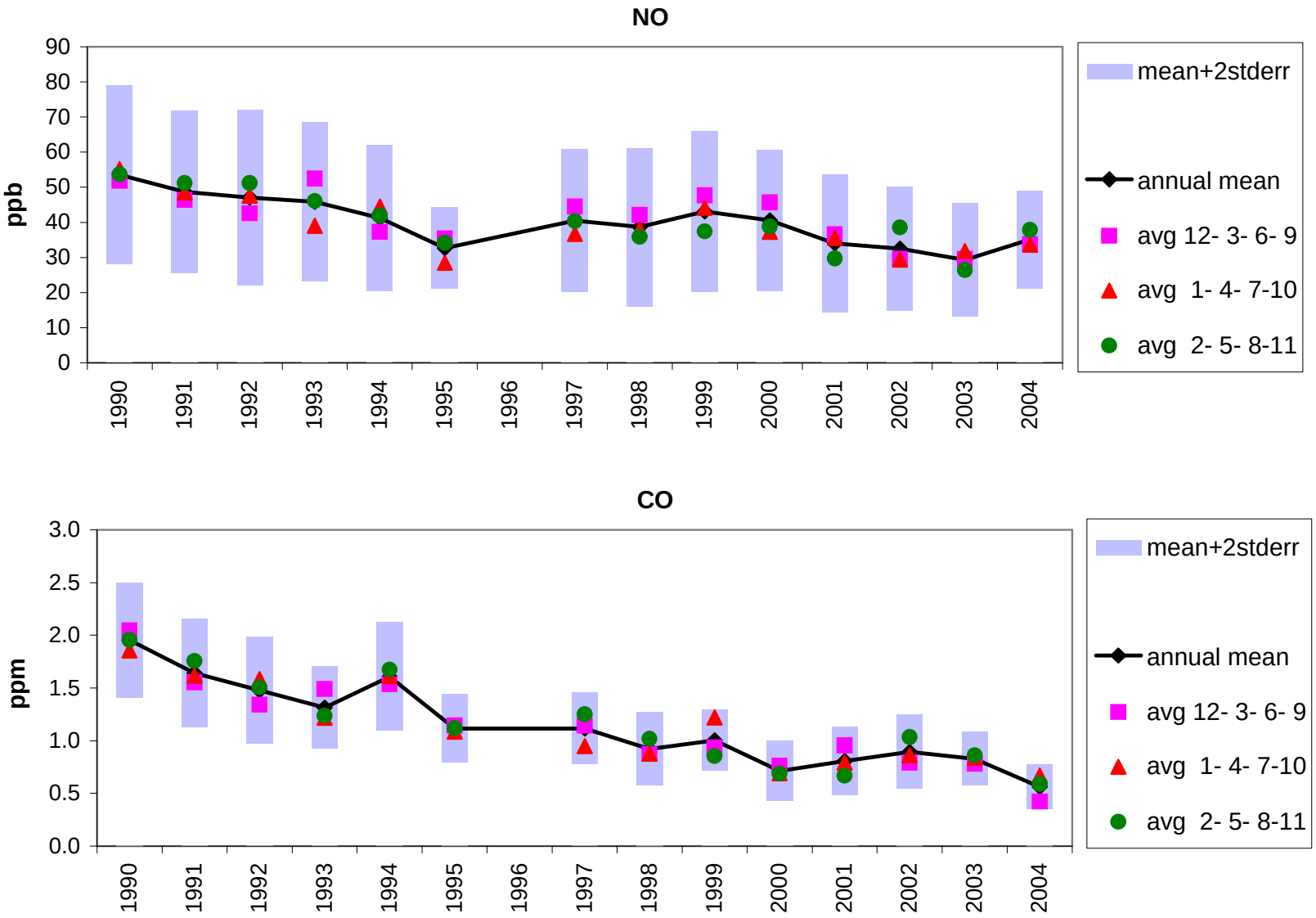


Source: UCLA and CARB

Harbor Community Monitoring Study
Saturation Monitoring

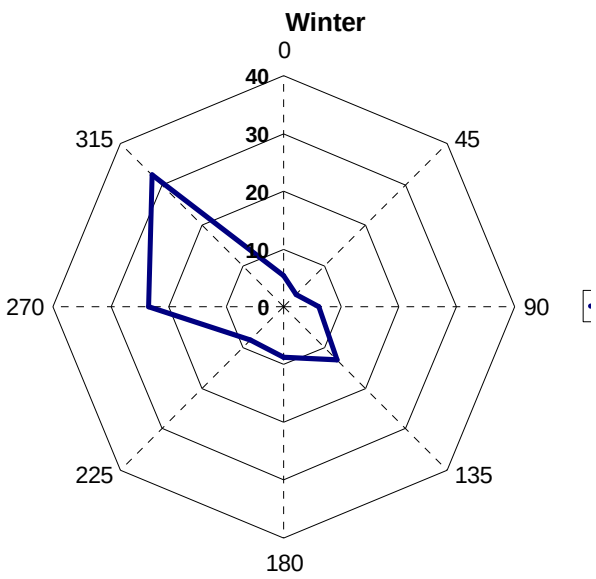
- **Monitoring Periods – 4 Weeks in 4 Seasons**
  - 2/13/07 to 3/13/07 (winter)
  - 5/15/07 to 6/12/07 (spring)
  - 7/31/07 to 8/28/07 (summer)
  - 11/13/07 to 12/11/07 (fall)

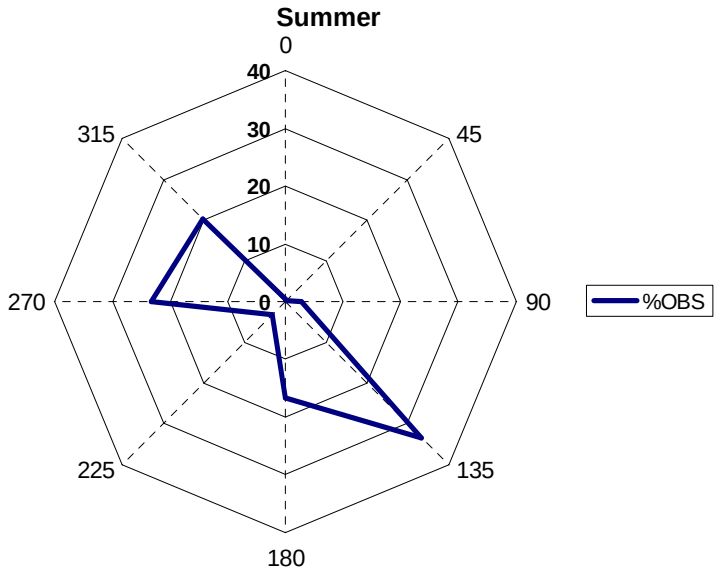
Annual Means of the Twelve Monthly Mean NO and CO versus Means of Four Months from Each Quarter – N. Long Beach

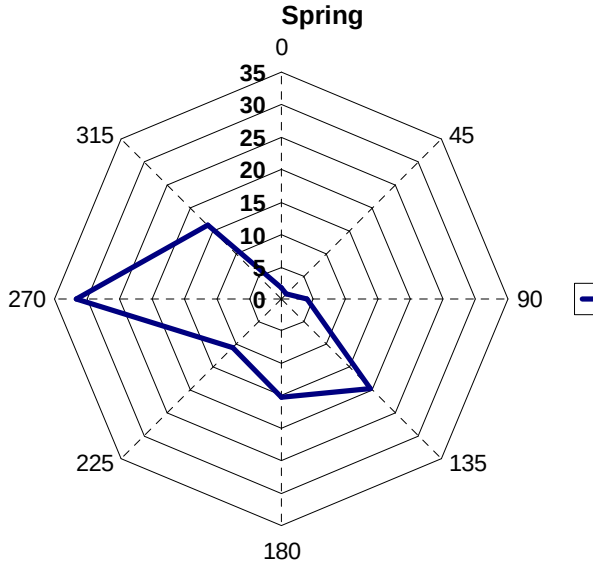


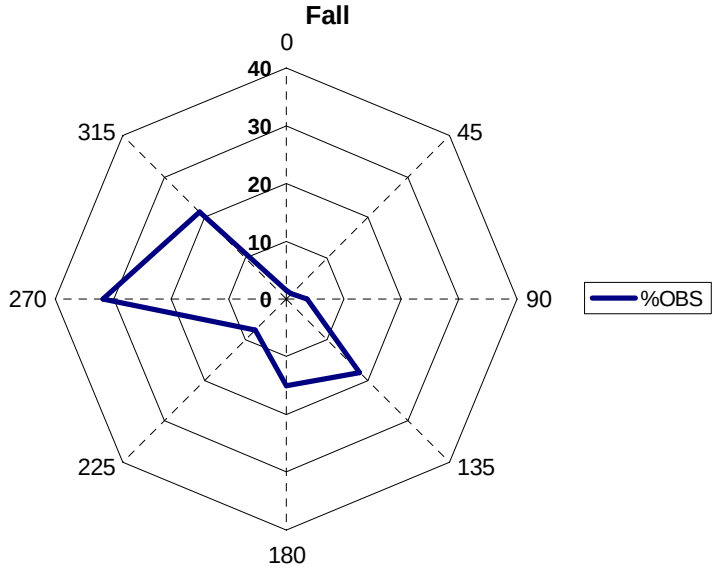
Seasonal wind patterns at Wilmington

August 2001-
July 2002



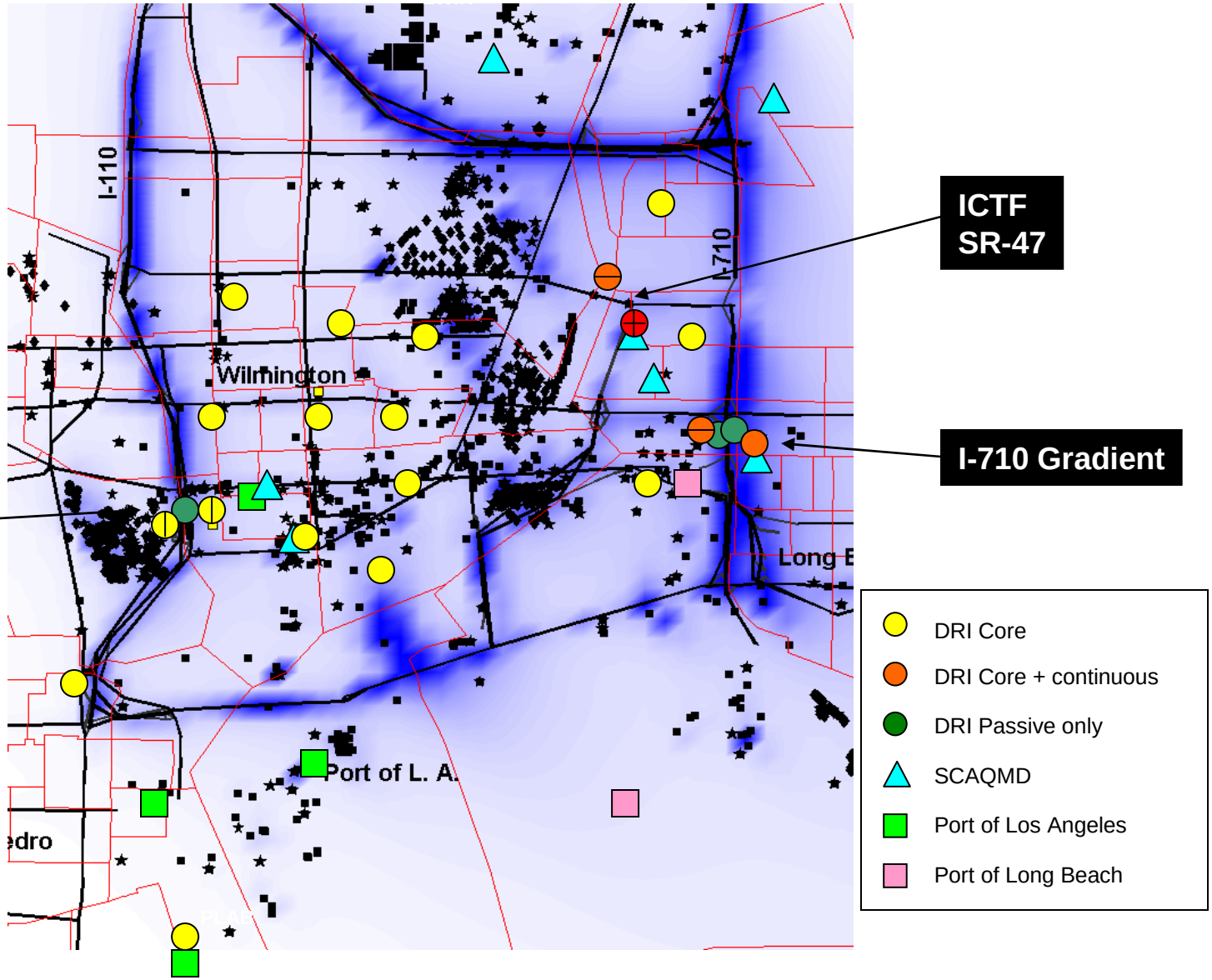






Winds predominately from W & NW and from the S and SE; rarely from the N, NE, and E

Locations of HCMS Sites on Spatial Mapping of ARB's Modeling Estimate of Annual Average DPM Concentrations



I-710 Gradient

Pacific Coast Hwy

Anaheim Street

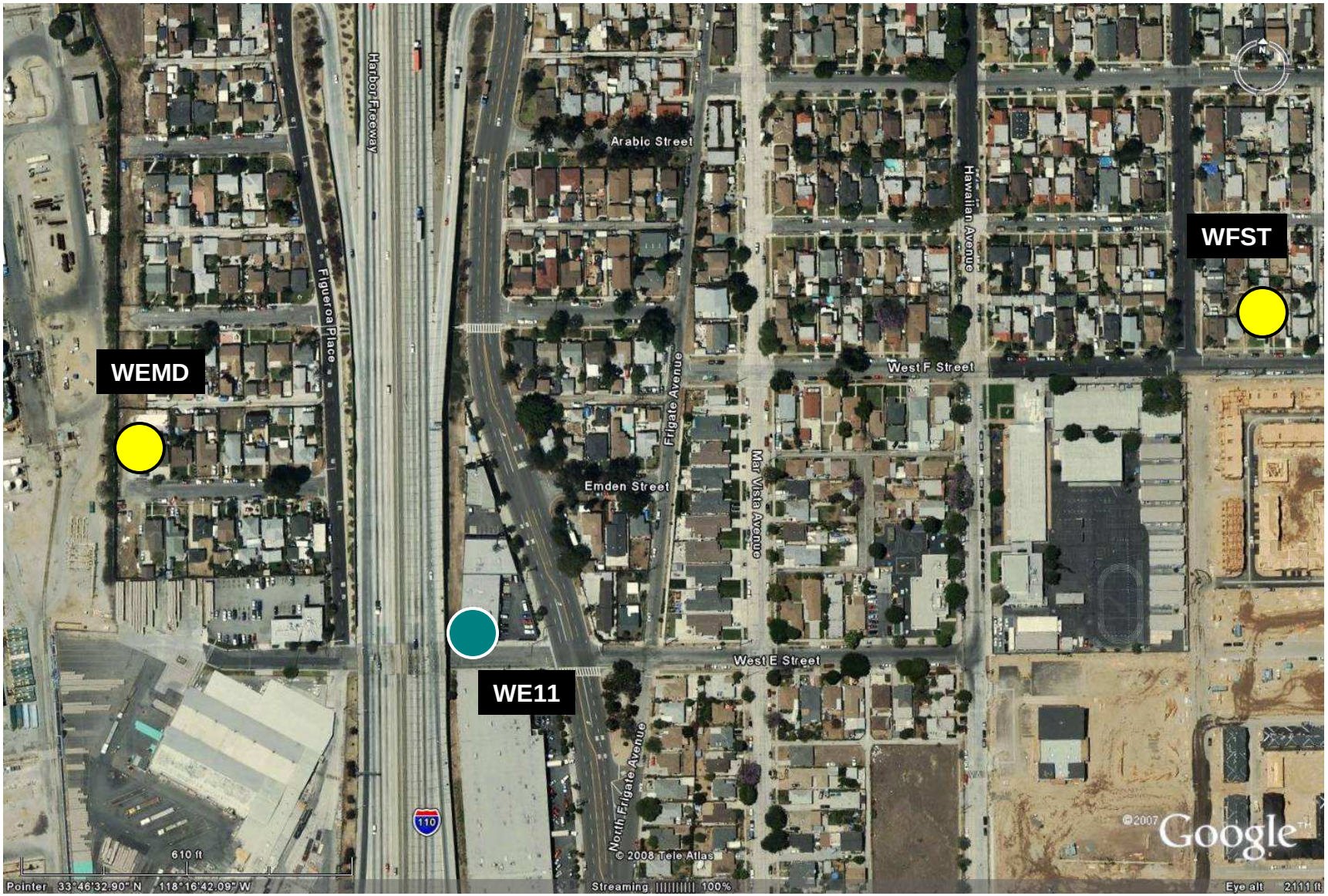
HCMS Sites Near the ICTF & Terminal Island Fwy

Terminal Island Freeway near the Intermodal Container Transfer Facility (ICTF)

HCMS Sites near Refinery & I-110

Anaheim Street

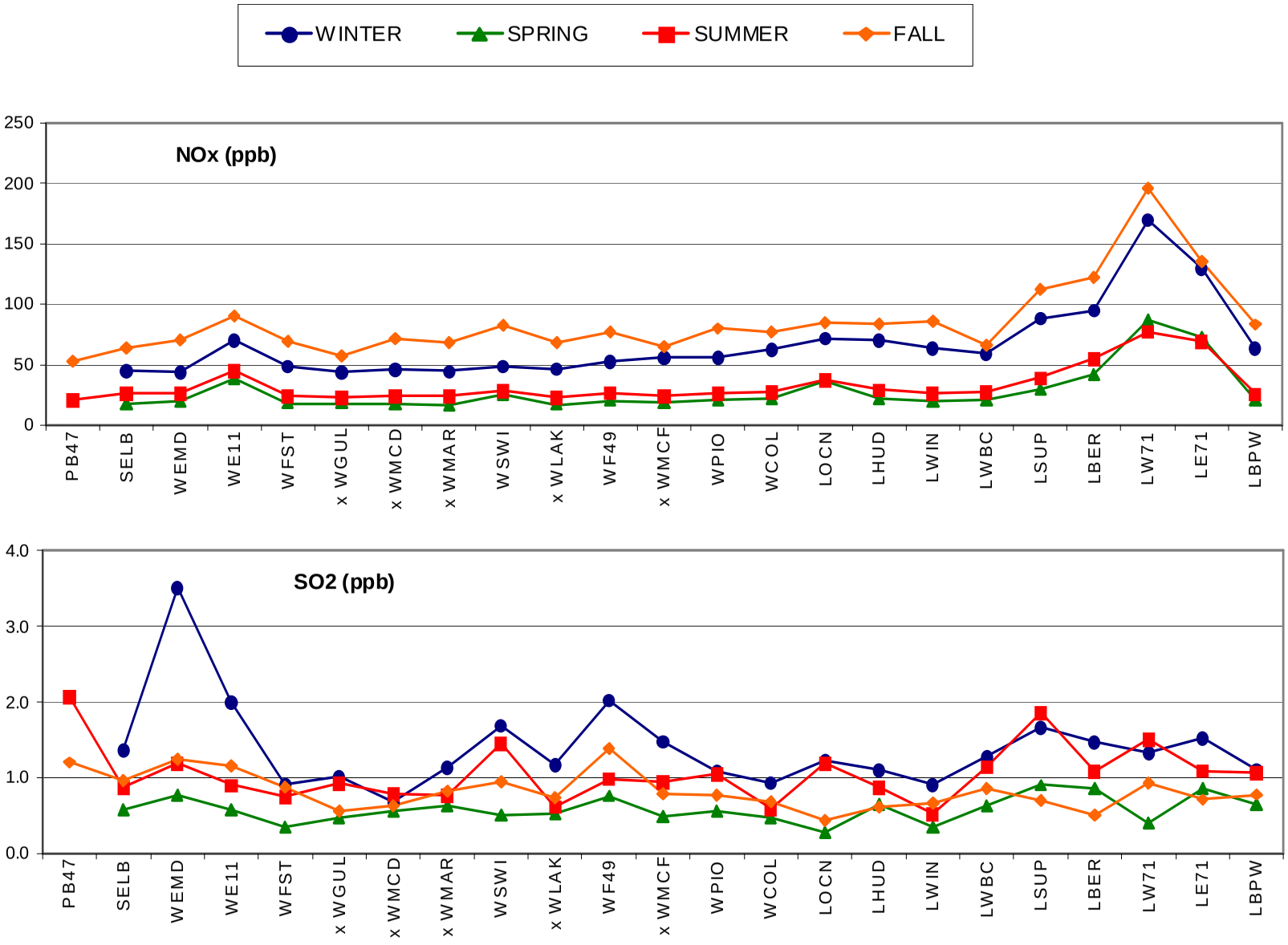
Refinery



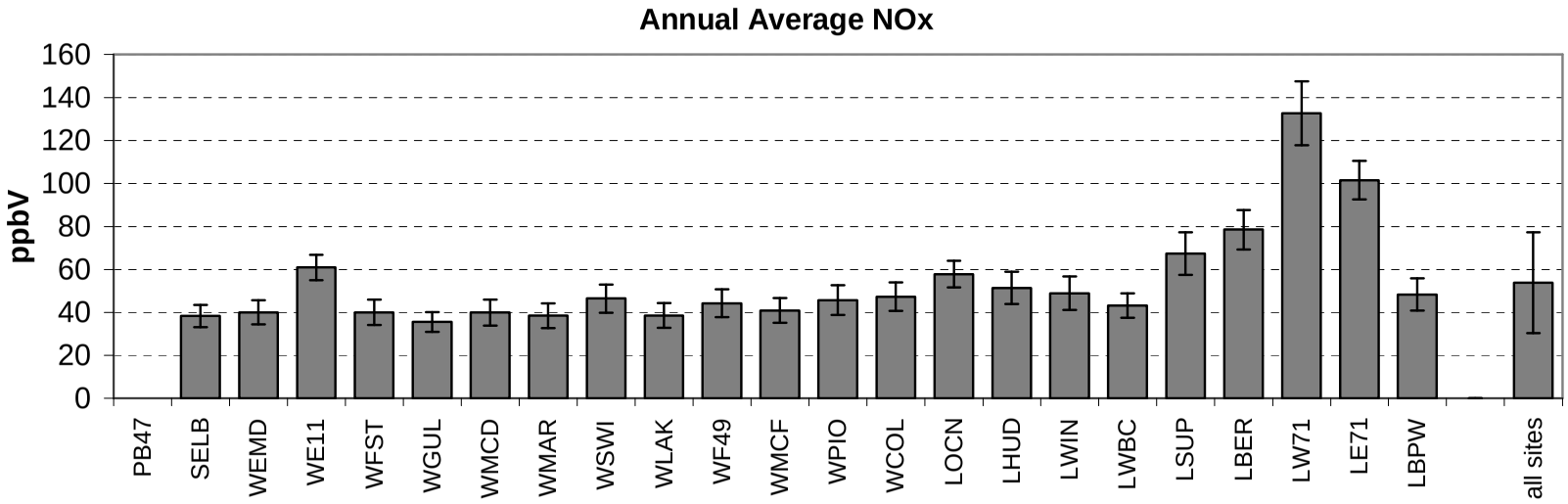
Overview of Presentation

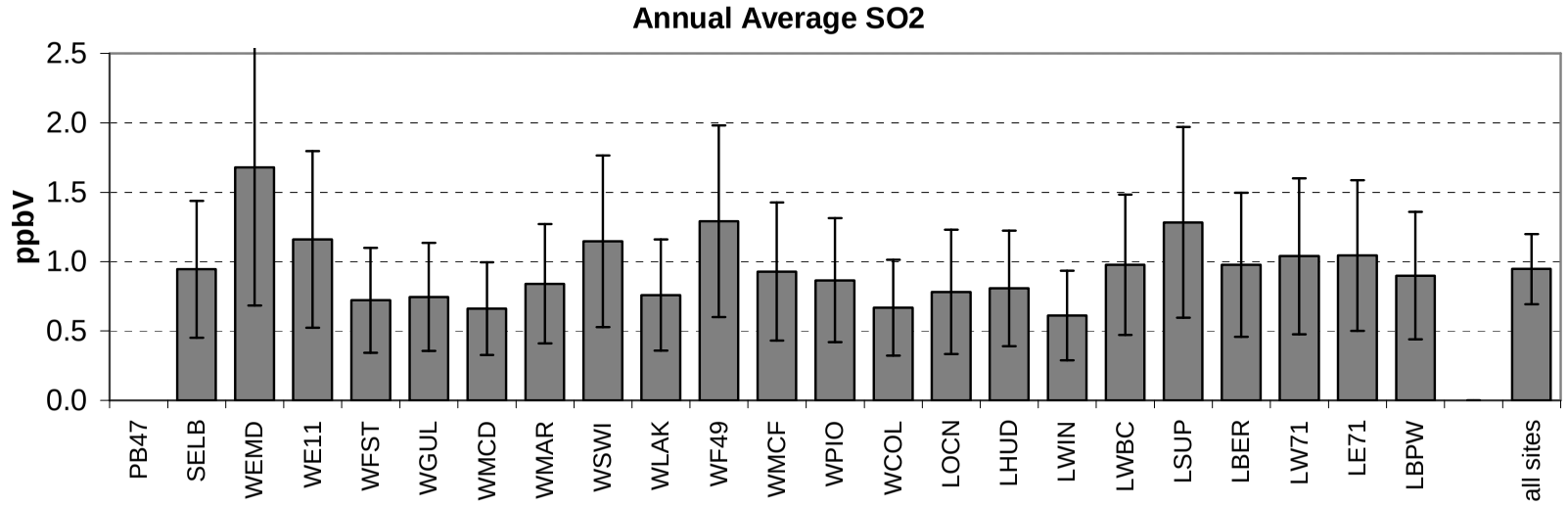
- Saturation monitoring objective.
- Passive monitoring methods. Laboratory and field evaluations.
- Saturation monitoring network design.
- **HCMS saturation monitoring results.**
- Comparisons of HCMS and MATES-III data and results from recent on-road and near-road studies.

Seasonal Averages for NO_x and SO_2



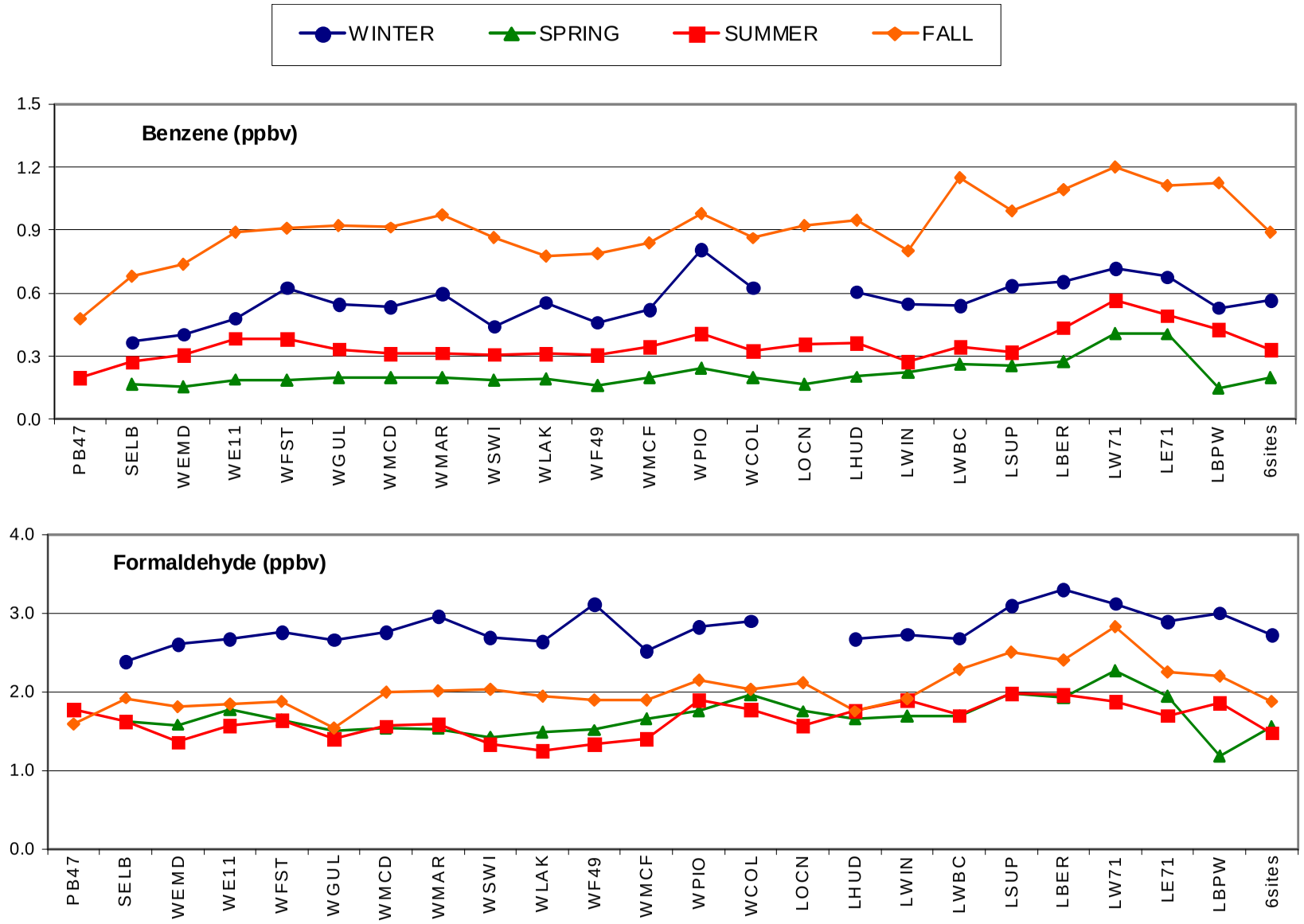
2007 HCMS Annual Mean NOx and SO_2



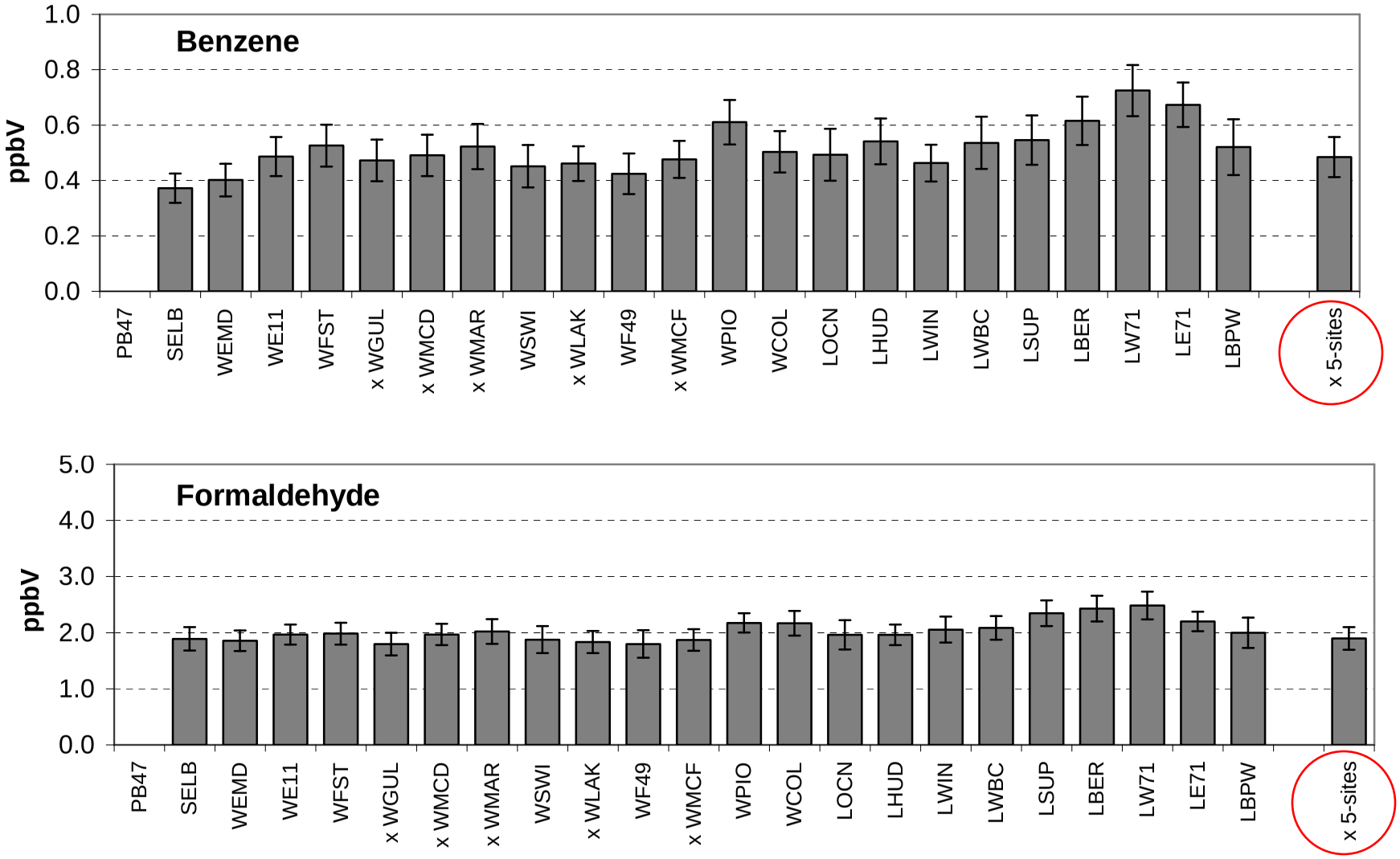


Uncertainty estimates are standard errors of the mean of 16 seven-day samples.

Seasonal Averages for Benzene and Formaldehyde

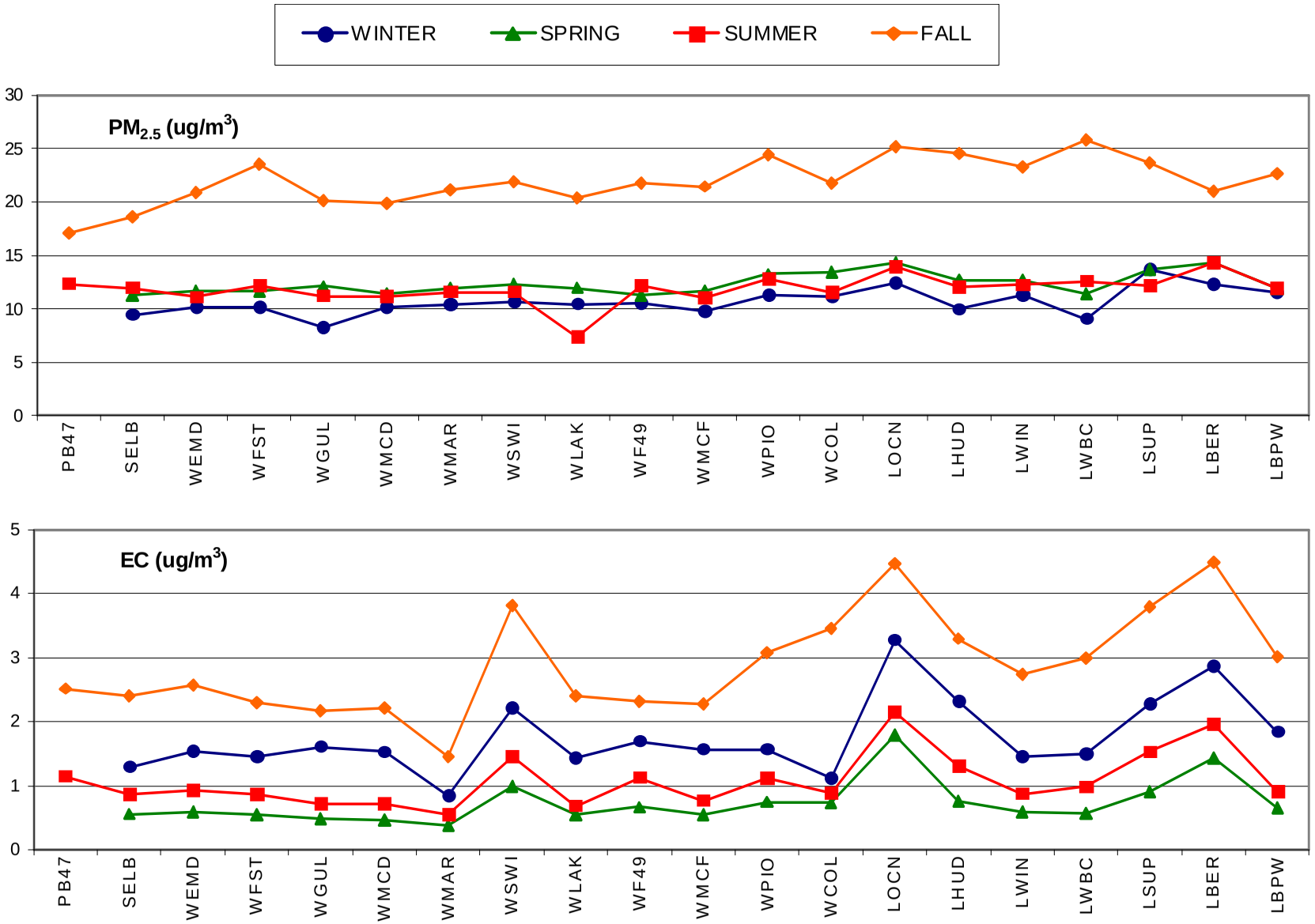


Annual Average Benzene and Formaldehyde (ppbv)

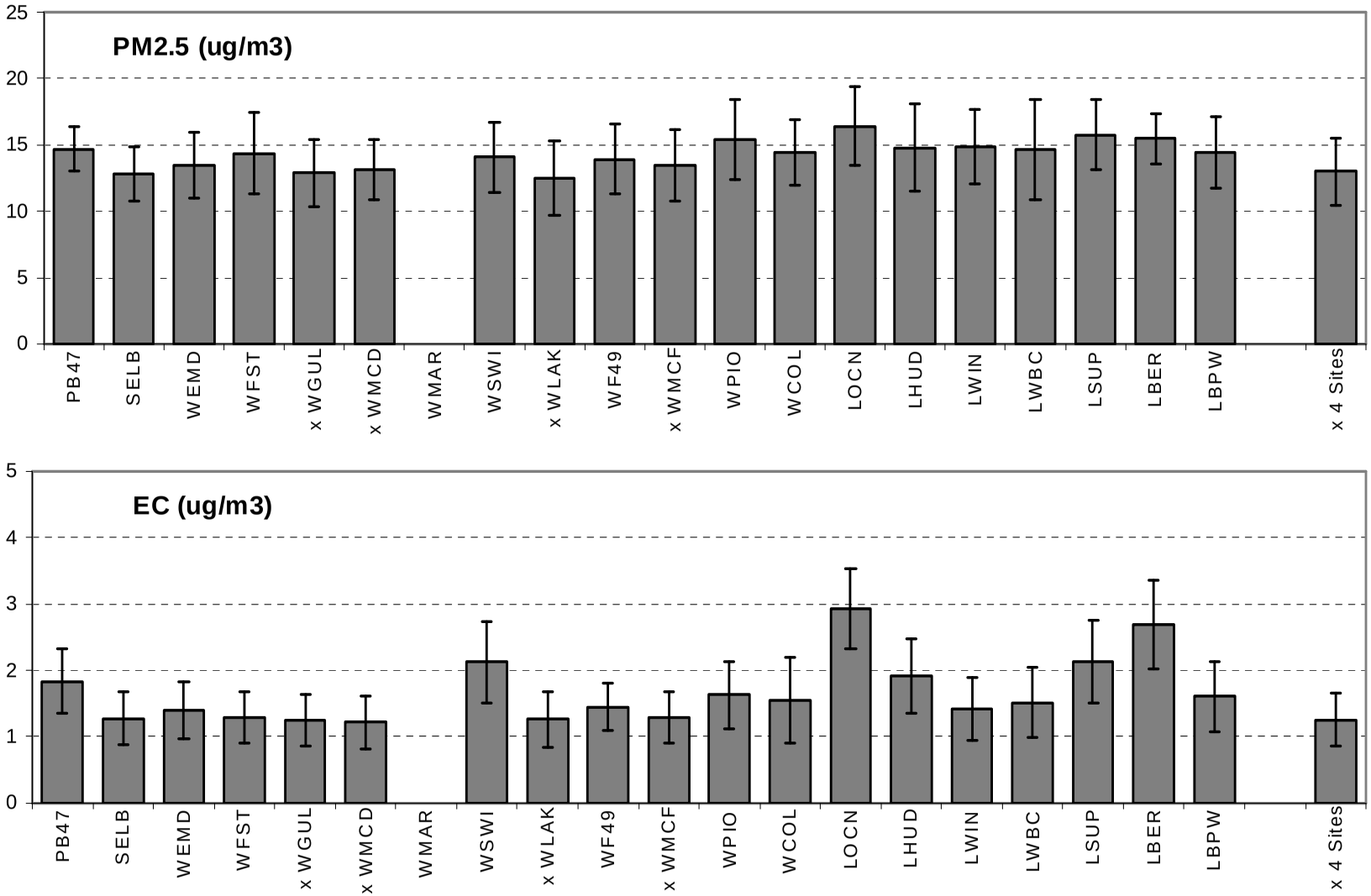


Uncertainty estimates are standard errors of the mean (n=up to 16).

Seasonal Average $PM_{2.5}$ and EC ($\mu g/m^3$)

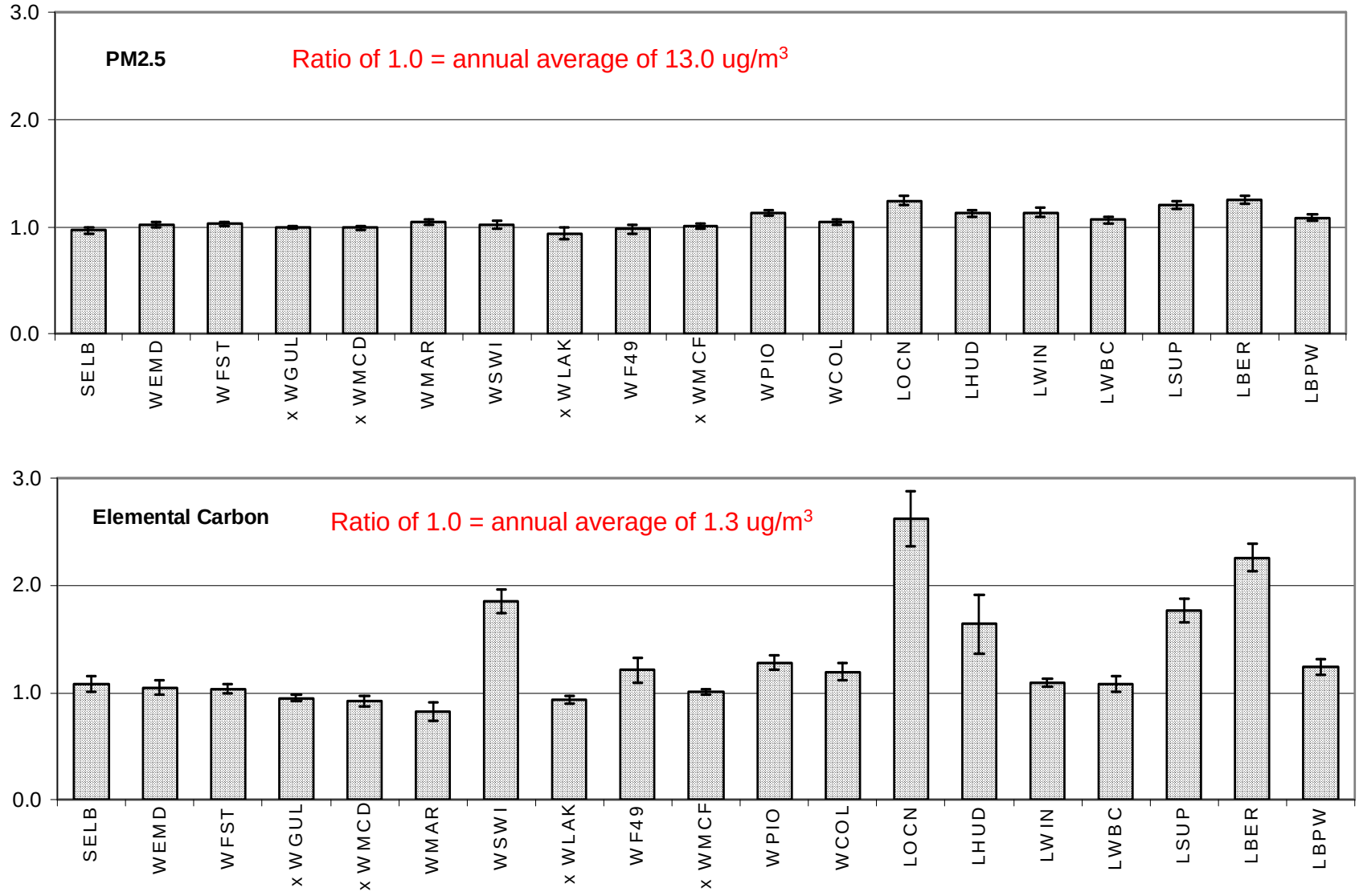


Annual Average $PM_{2.5}$ and EC (µg/m^3)

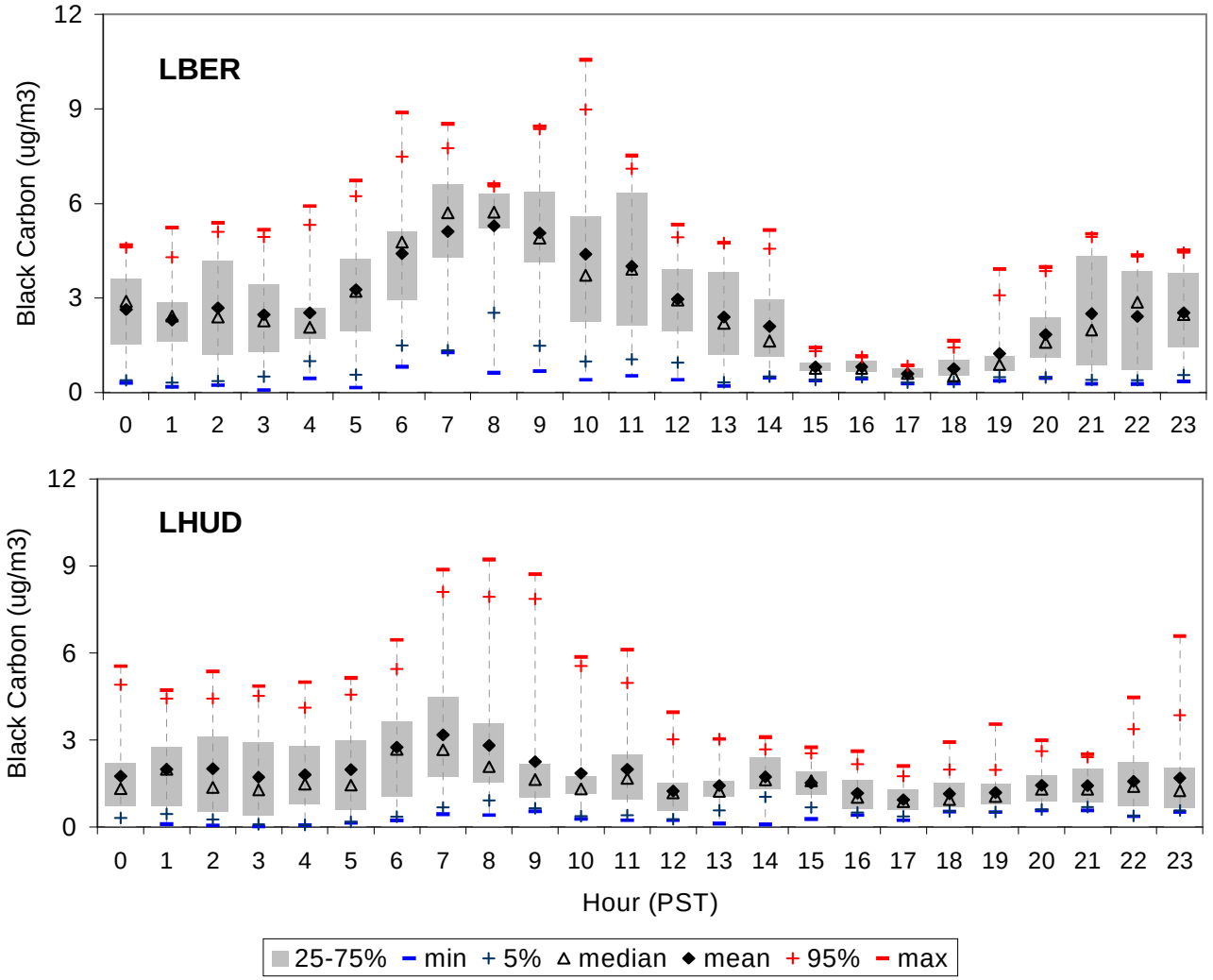


Uncertainty estimates are standard errors of the mean (n=up to 16).

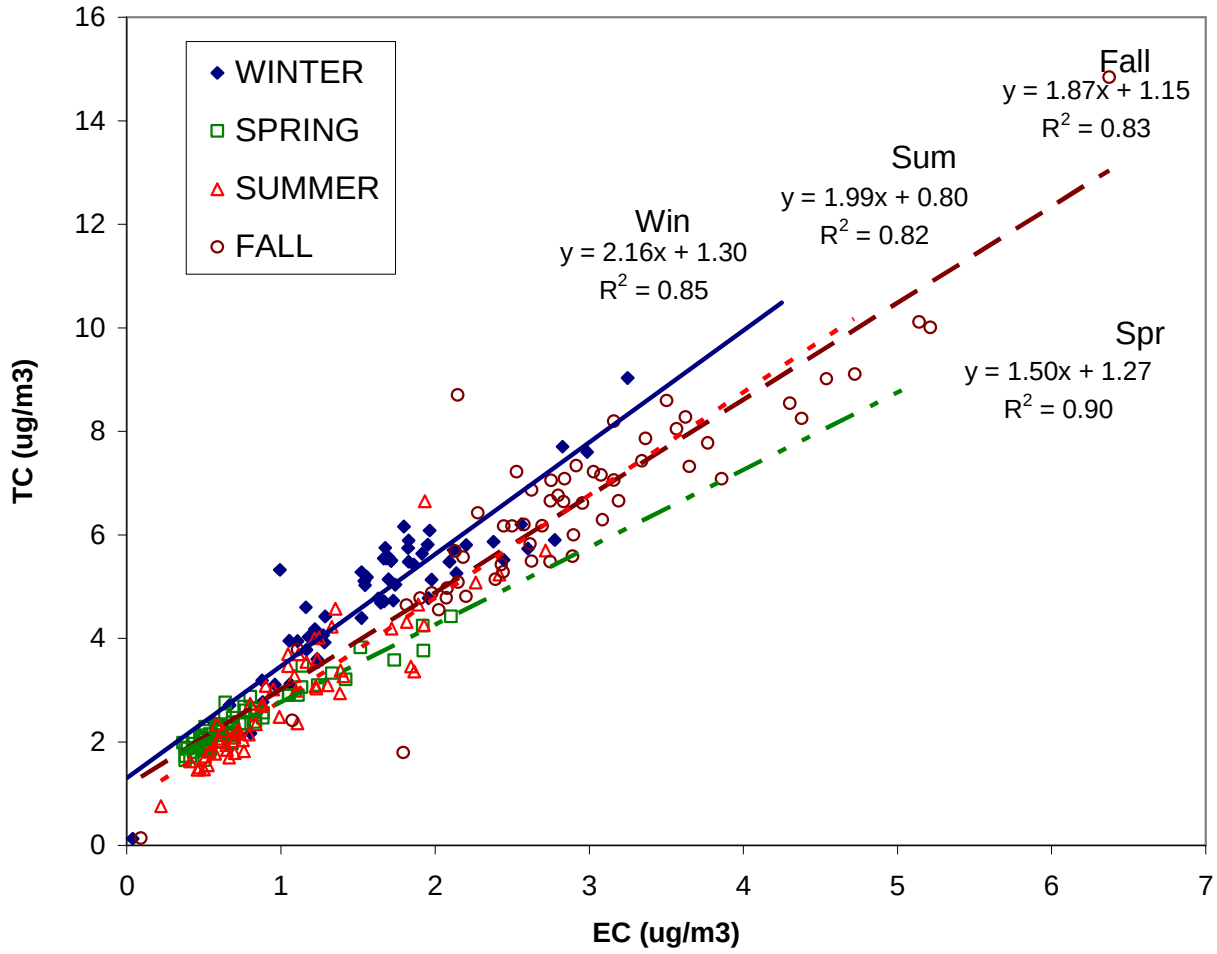
Mean ± SE of Ratios of EC and $PM_{2.5}$ to 4-Site Means



Diurnal Variations in Black Carbon, 2/13/07 to 3/13/07



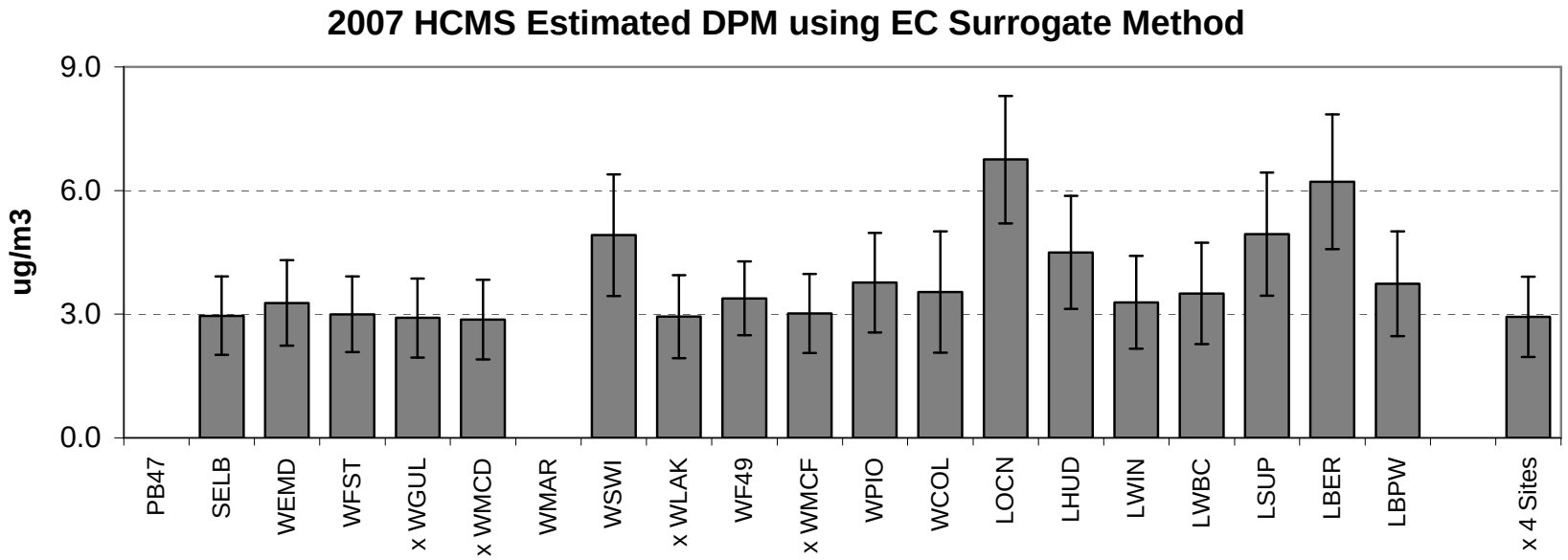
Correlation of TC and EC by Season

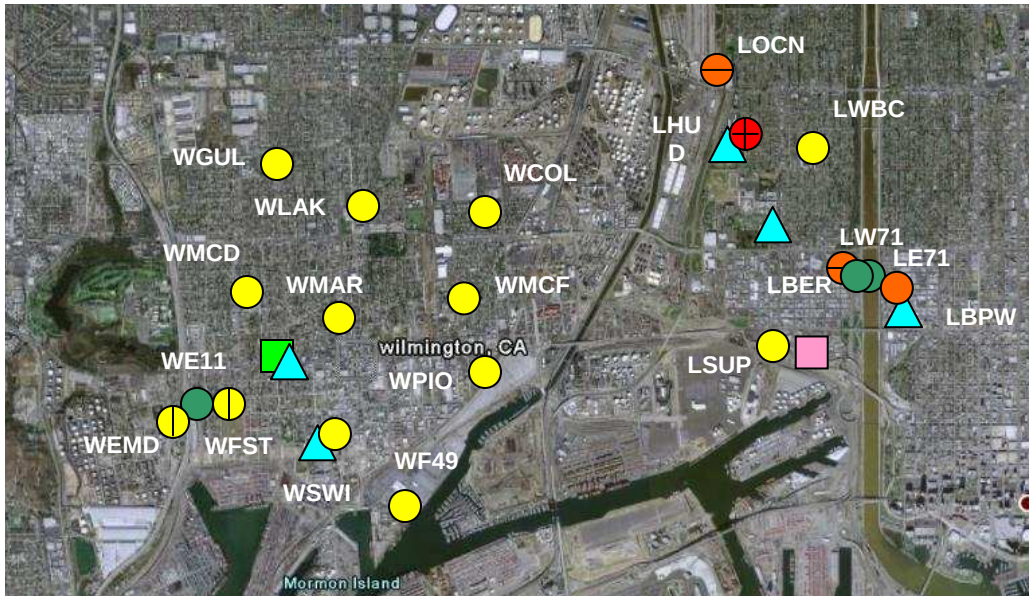


Diesel Particulate Carbon (DPC) = measured EC * slope of TC versus EC correlation

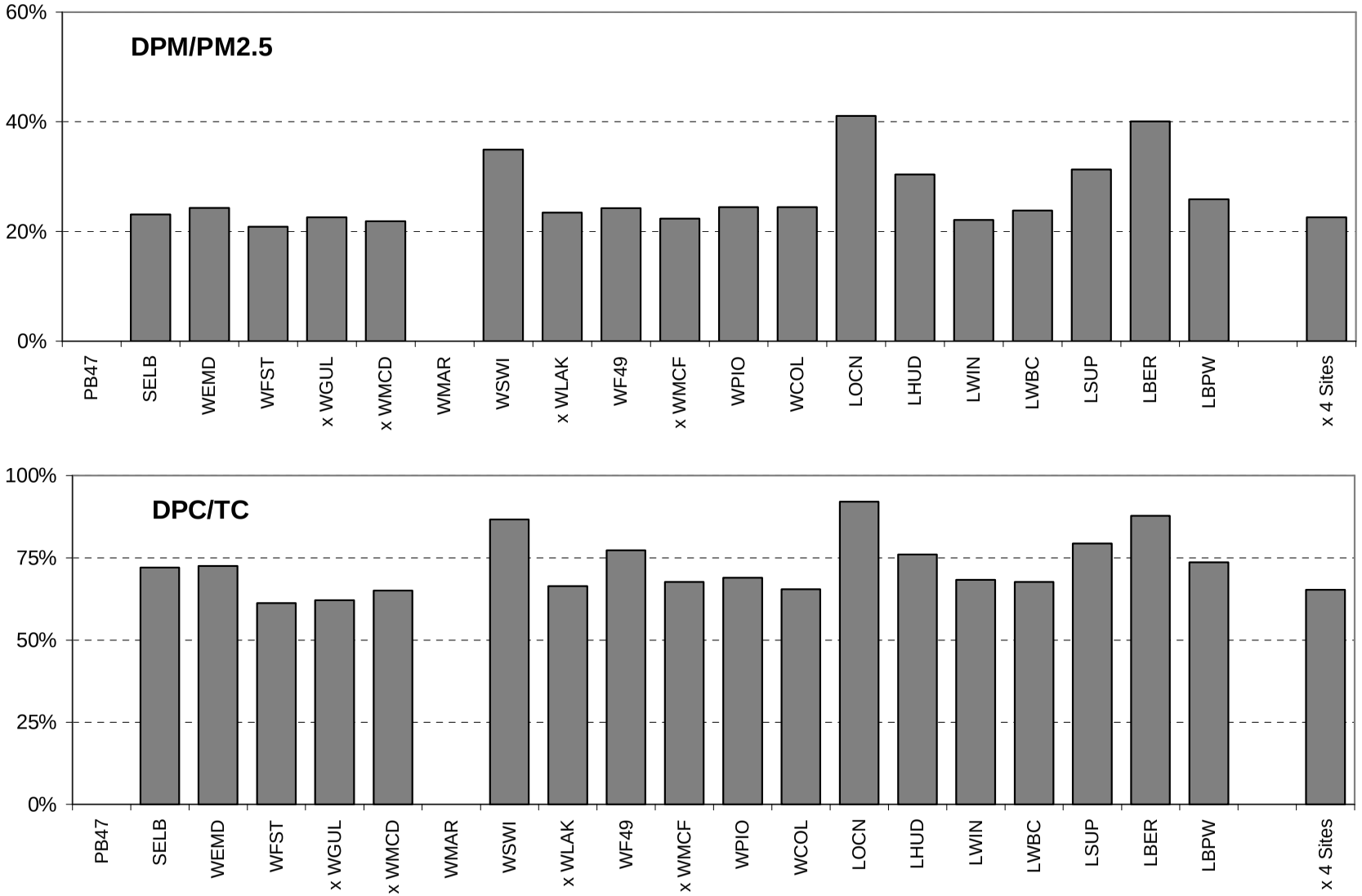
Diesel Particulate Matter (DPM) = EC + 1.46 (DPC-EC)

Annual Average Diesel PM Concentrations





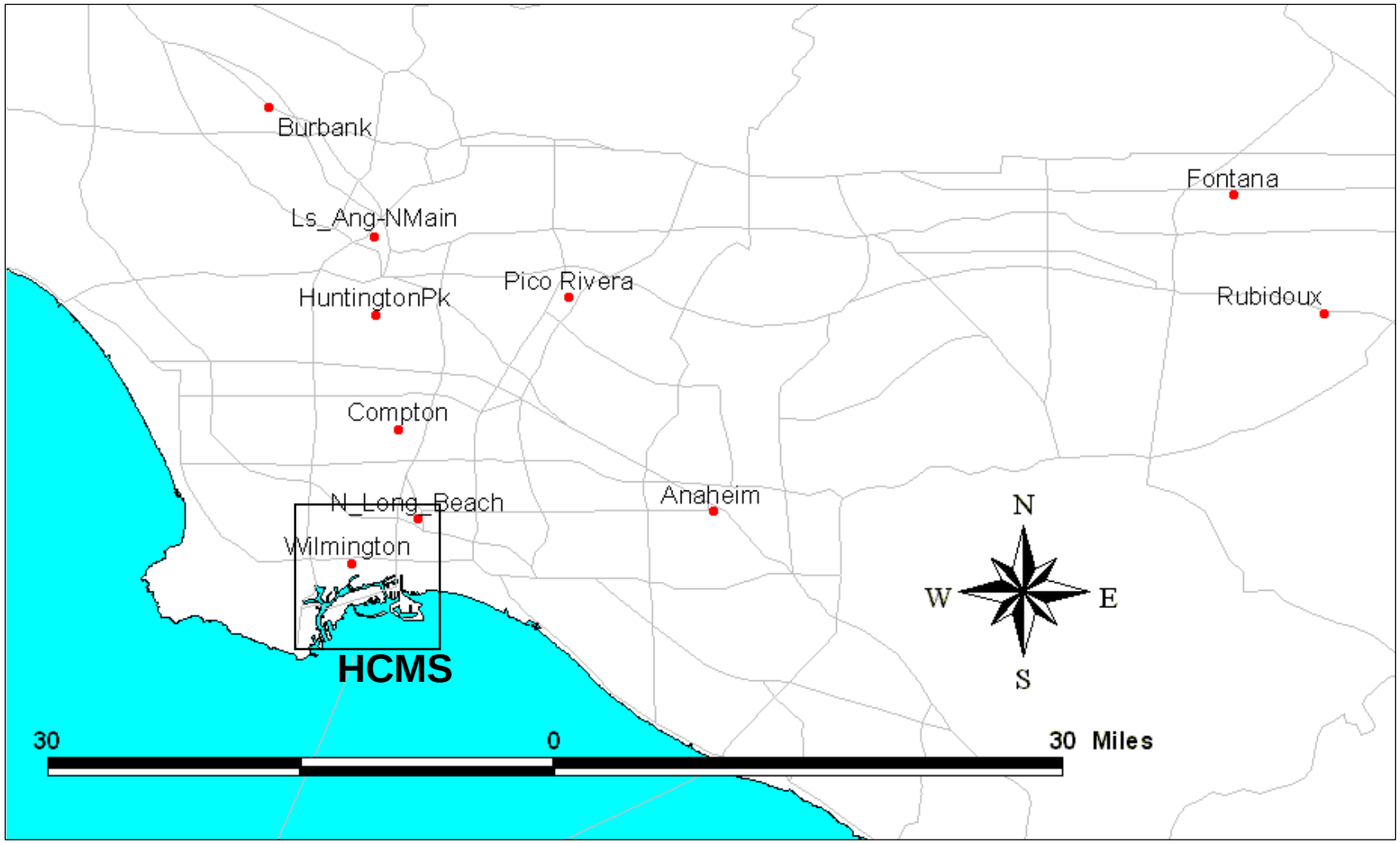
Annual Average DPM/$PM_{2.5}$ and DPC/TC mass ratios



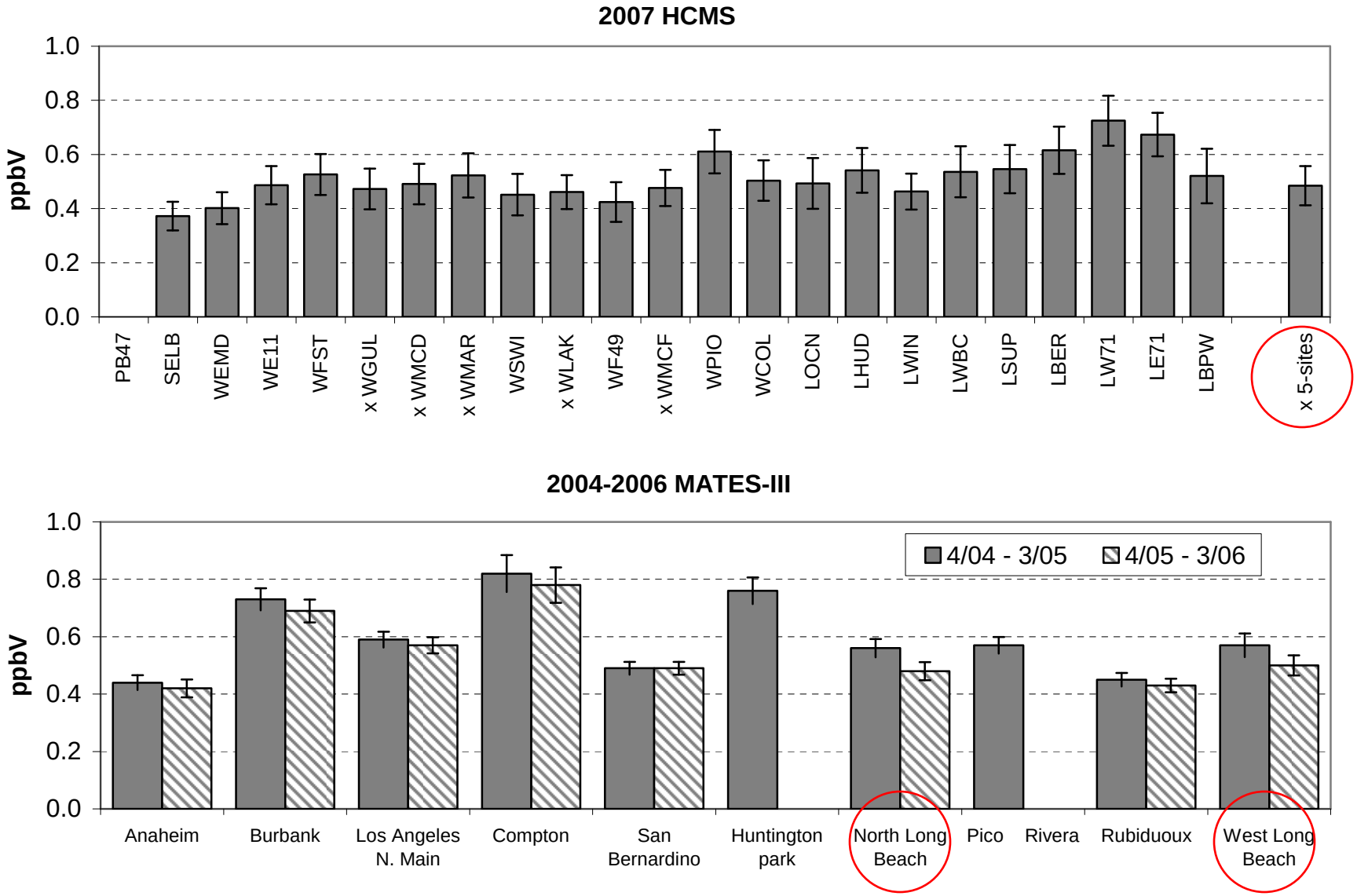
Overview of Presentation

- Saturation monitoring objective.
- Passive monitoring methods. Laboratory and field evaluations.
- Saturation monitoring network design.
- HCMS saturation monitoring results.
- **Comparisons of HCMS and MATES-III data and results from recent on-road and near-road studies.**

MATES-III Fixed Monitoring Sites, 4/04 to 3/06

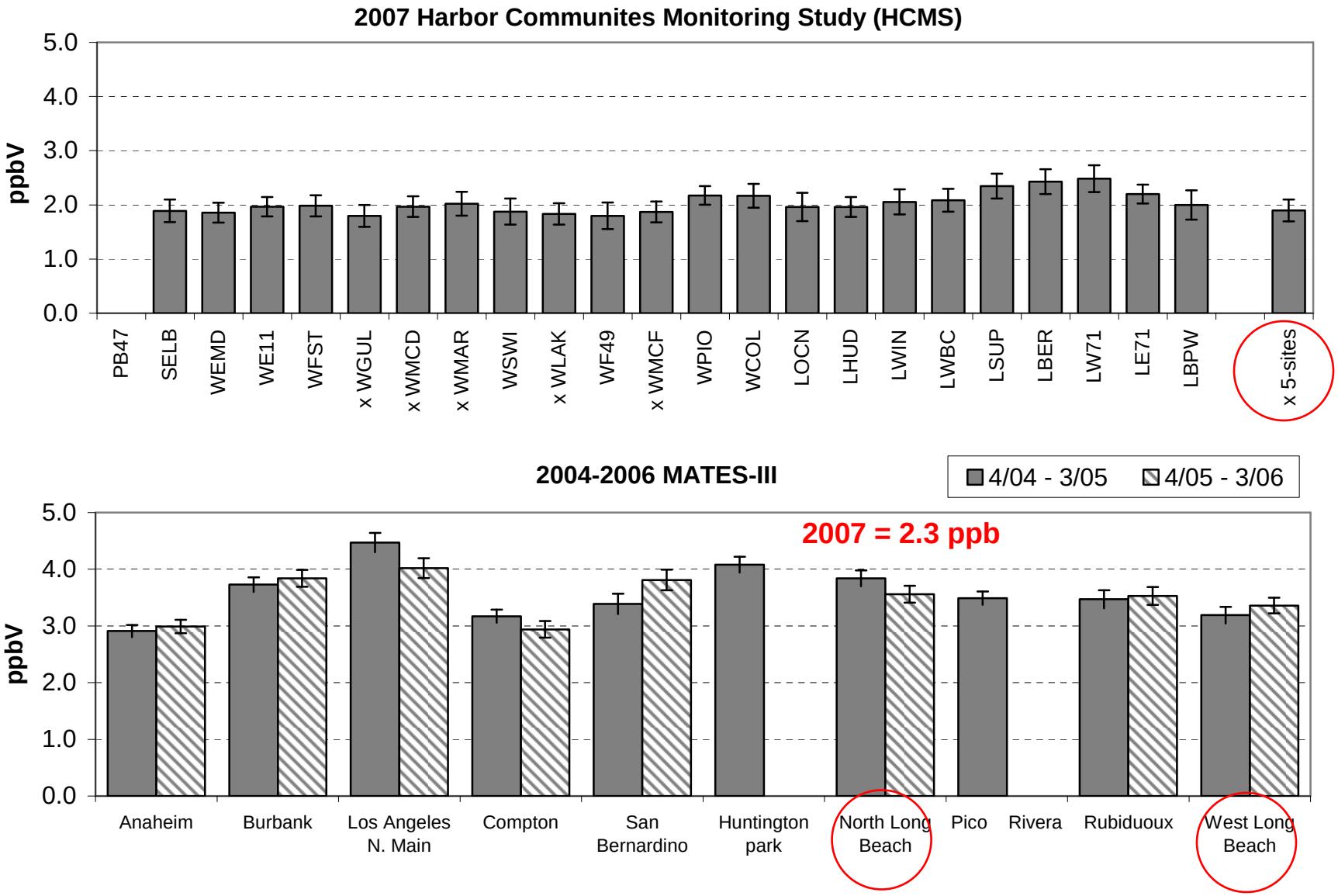


Annual Average Benzene (ppbv)



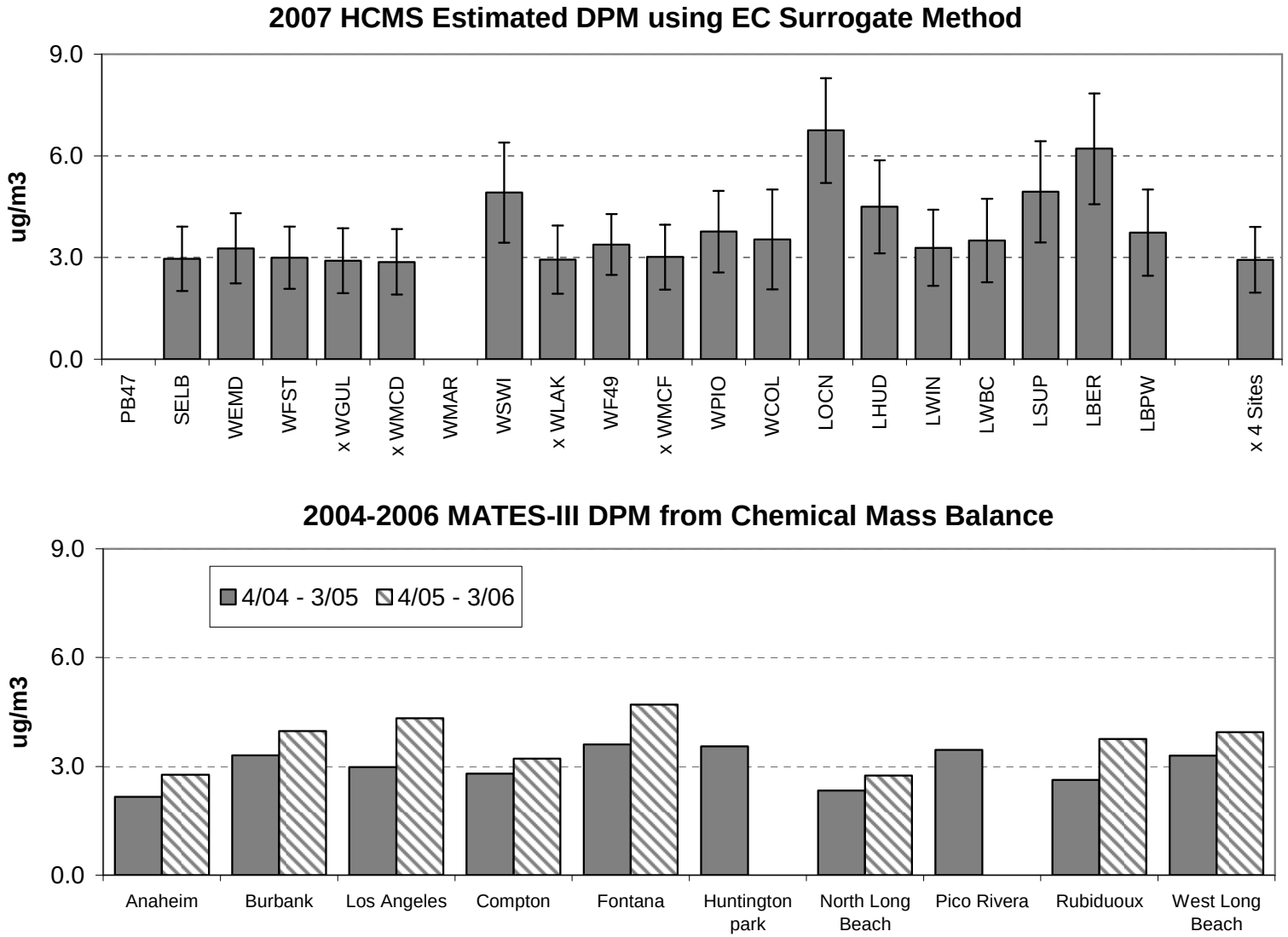
Uncertainty estimates are standard errors of the mean (n=up to 16 for DRI and up to 121 for SCAQMD).

Annual Average Formaldehyde (ppbv)



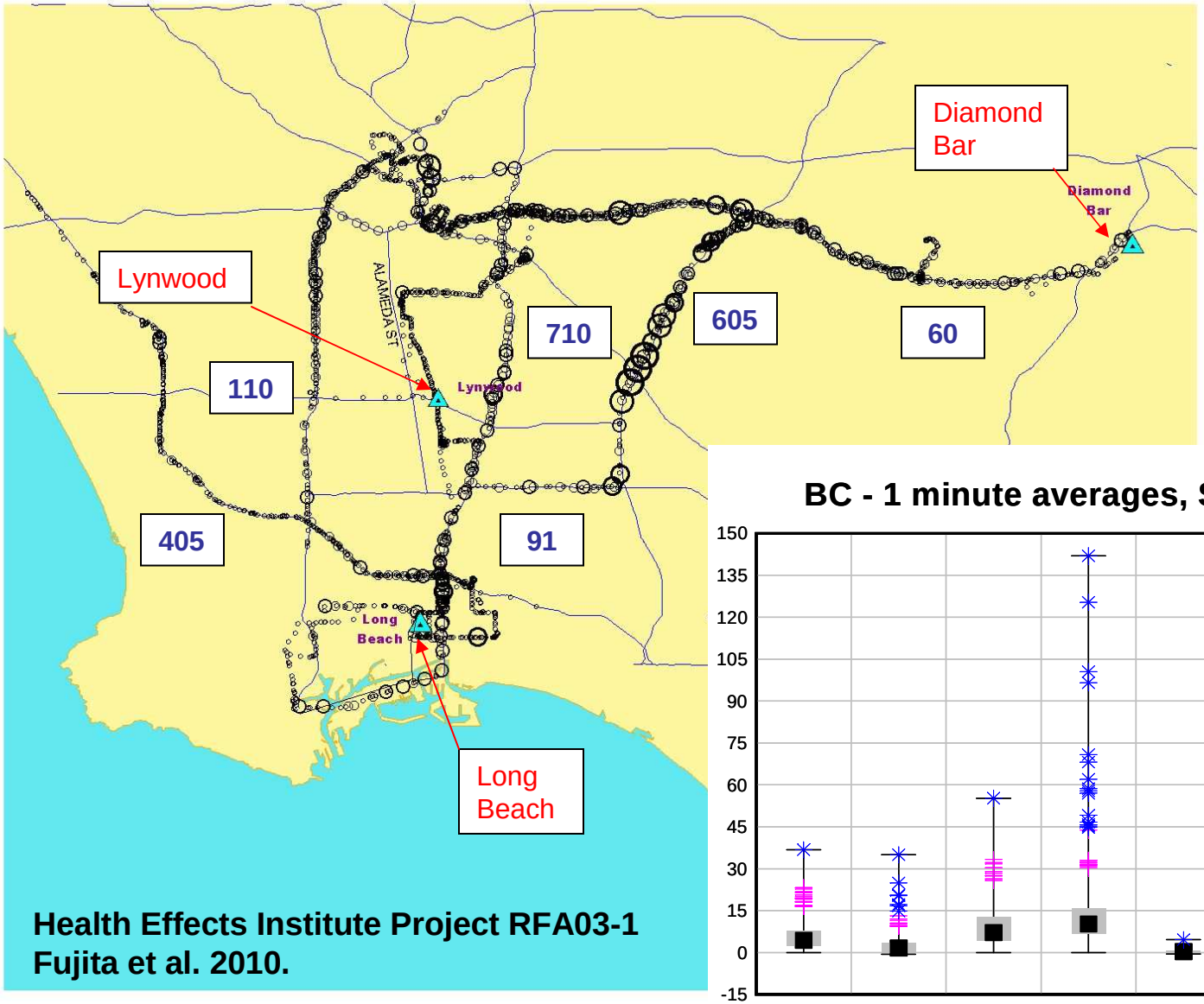
Uncertainty estimates are standard errors of the mean (n=up to 16 for DRI and up to 121 for SCAQMD).

Annual Average Diesel PM Concentrations



Uncertainty estimates are standard errors of the mean (n = four seasonal means for DRI).

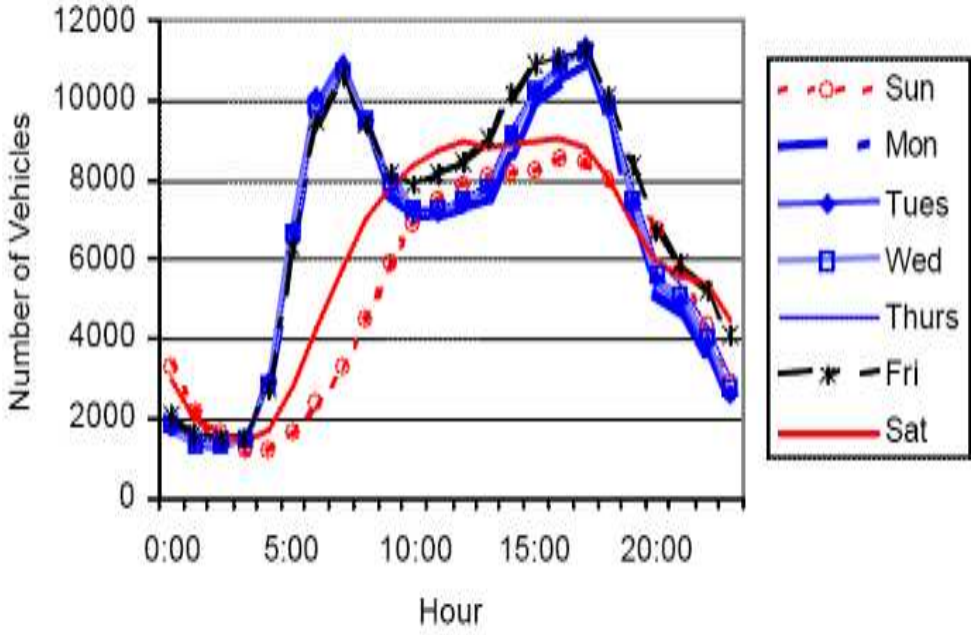
On-Road Black Carbon Concentrations by Photoacoustic



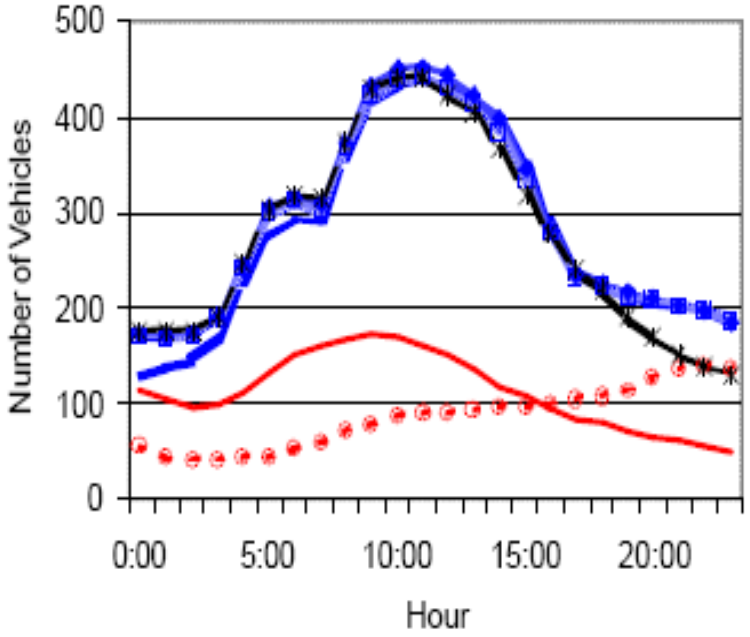
Sept. BC (ug/m3)
- 0 - 10
- 10 - 20
- 20 - 40
- 40 - 60
- 60 - 100
- 100 - 150
- Freeways
- shoreline

Average Hourly Light-Duty and Heavy-Duty Traffic Volumes Weigh-in-Motion Sites in Interior of South Coast Air Basin

Light-Duty

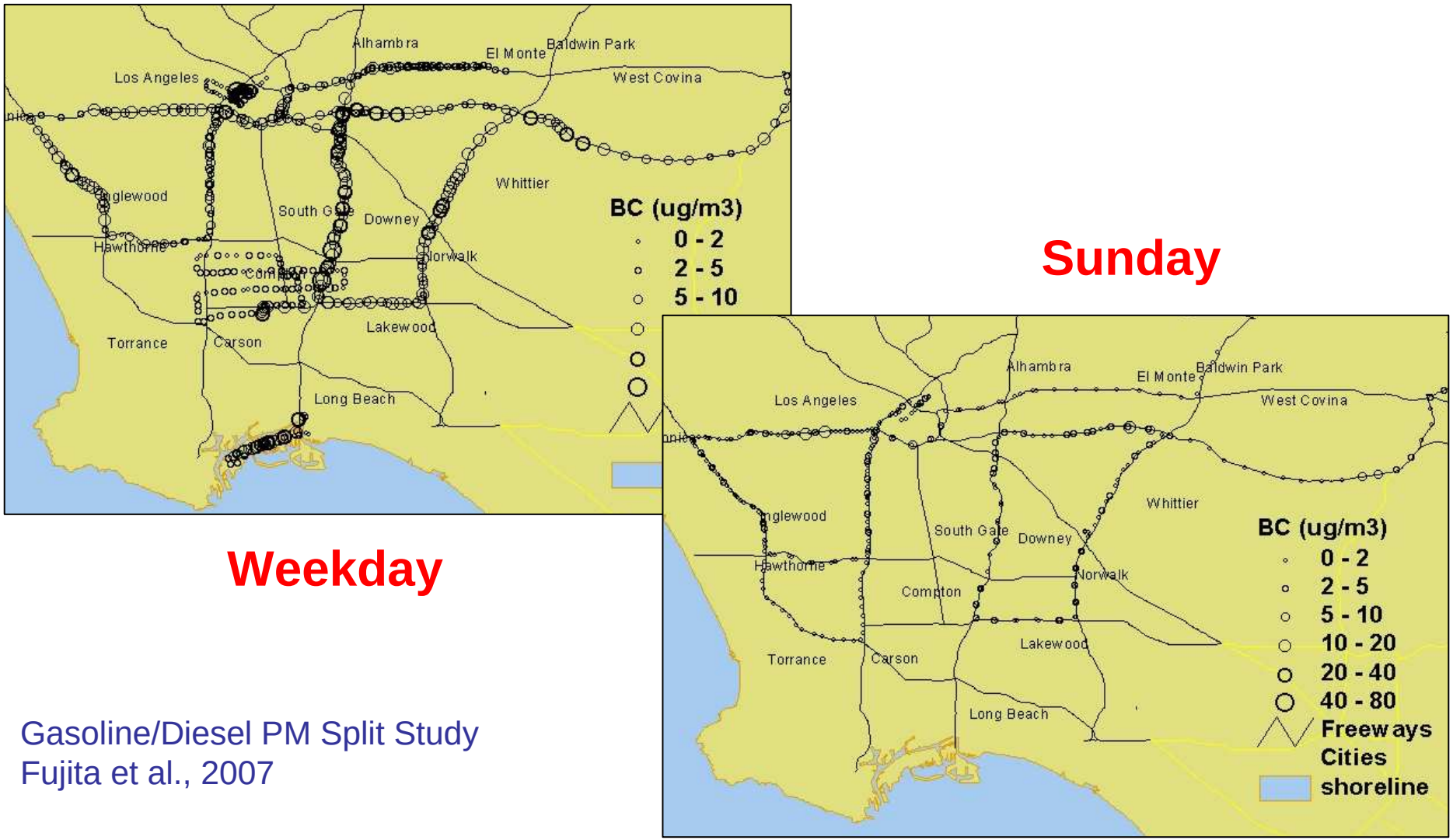


Heavy-Duty



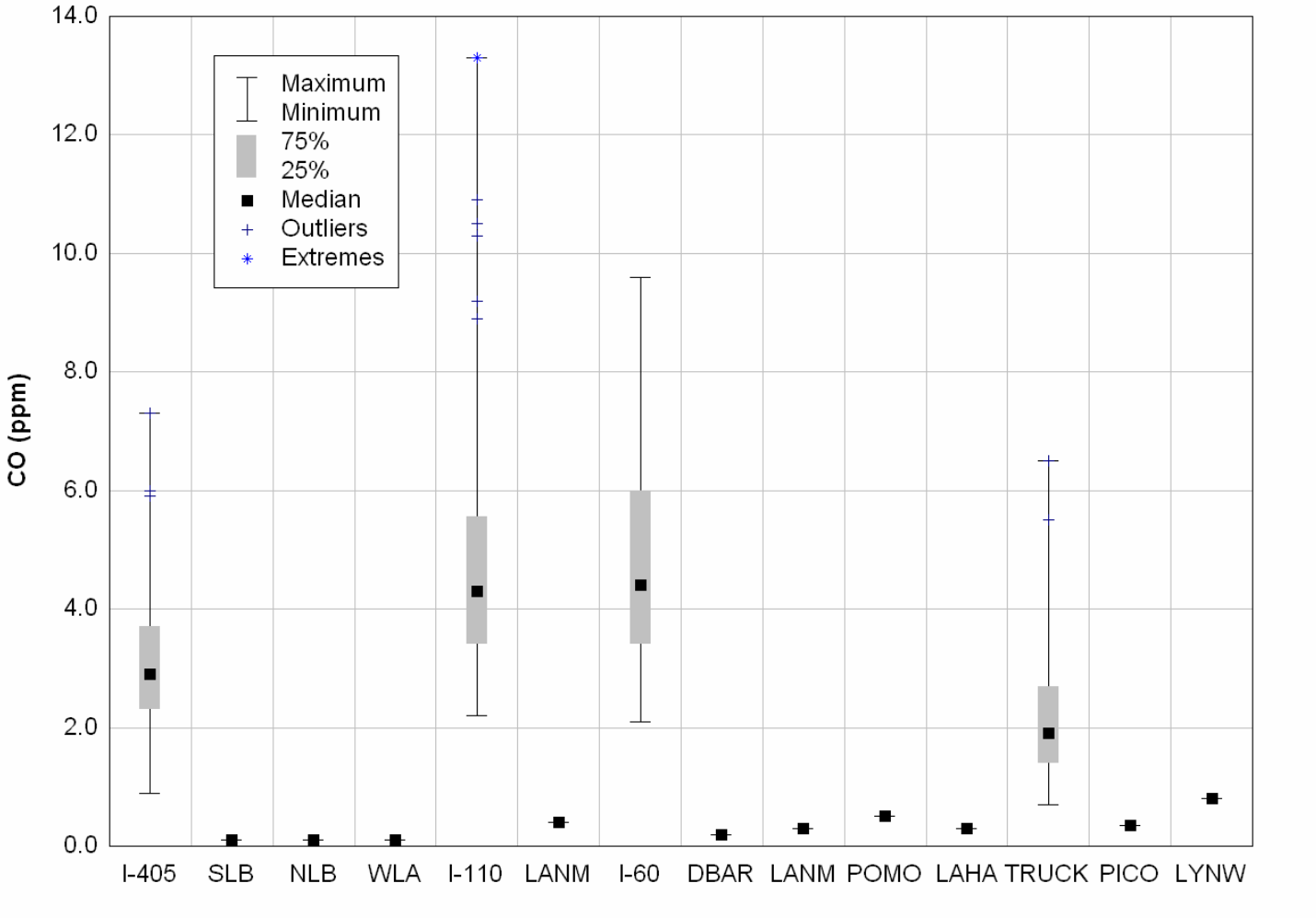
DOE NREL Weekend Ozone Study
Courtesy of Sonoma Technology, Inc., 2002

Photoacoustic Black Carbon (1-minute averages)



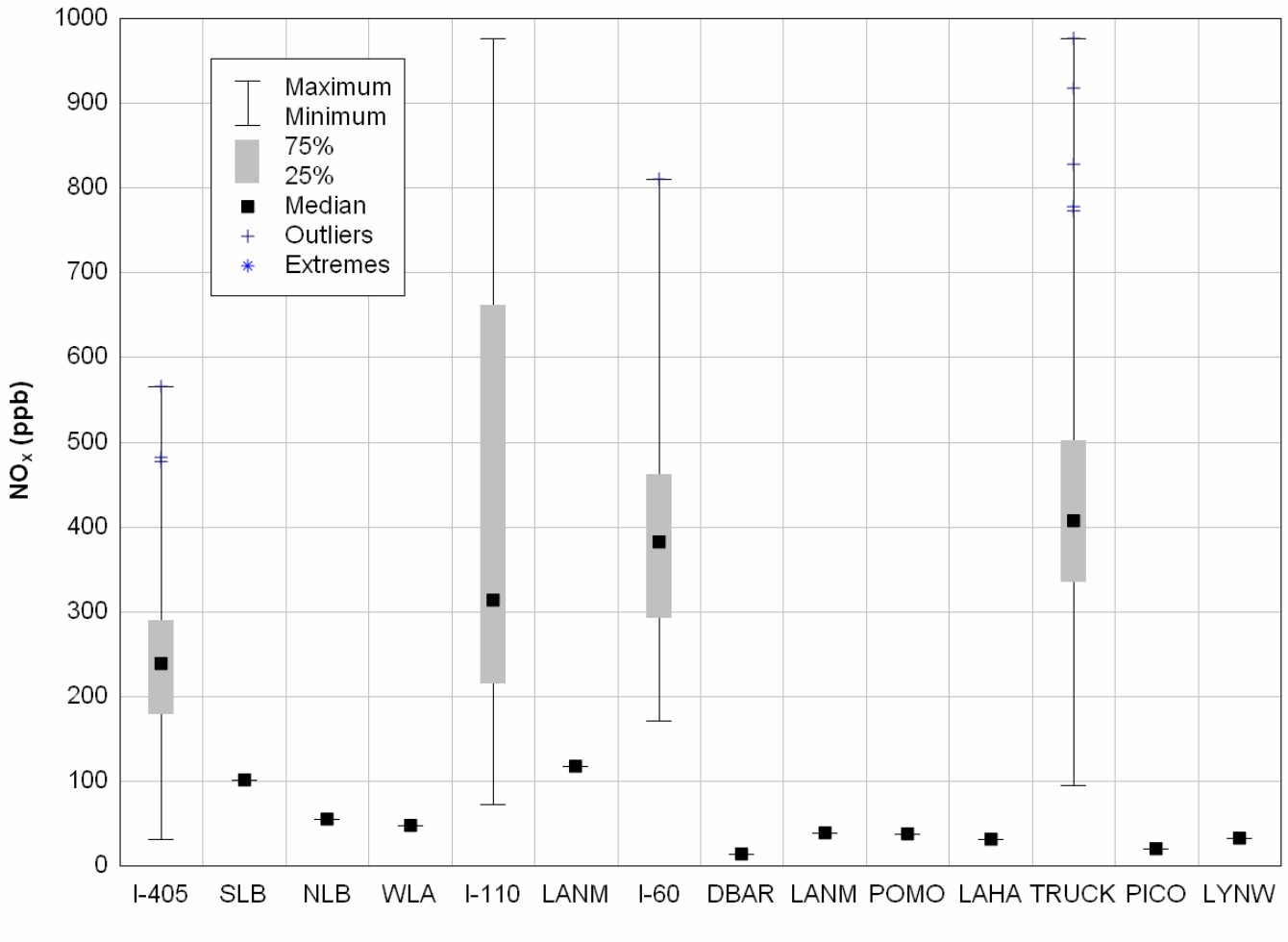
Gasoline/Diesel PM Split Study
Fujita et al., 2007

Comparisons of On-Road Versus Fixed Station Summer Morning CO



Health Effects Institute Project RFA03-1
Fujita et al. 2010

Comparisons of On-Road Versus Fixed Station Summer Morning NOx



Health Effects Institute Project RFA03-1
Fujita et al. 2010

Summary of Results

- Higher average SO_2 levels at the east boundary of the Conoco Refinery and in the port area (max site = 1/20th of NAASQ). However corresponding increases in BTEX were not observed near the refinery.
- Slightly higher levels of BTEX and aldehydes near roadways, but spatial variations were relatively small within study area.
- NOx and EC concentrations were 2 to 4 times higher near diesel truck traffic. Sharp gradient away from roadway. Results are qualitatively consistent with the ARB's modeling estimates of DPM concentrations.
- Annual average DPM concentrations were up to two times higher near diesel truck traffic and were comparable to the rest of the basin at locations 300 m or more from traffic.
- On an annual average, DPM is about 20% of $PM_{2.5}$ at community sites and about 40% at location in close proximity to truck traffic.
- Spatial variations in annual average $PM_{2.5}$ concentrations were much less than NOx and EC (and DPM).

HCMS Saturation Monitoring Hypotheses

1. Passive monitoring methods have sensitivity and precision comparable to conventional monitoring methods (averaged over the same period). *Generally true with few exceptions.*

- Radiello and Ogawa passive samplers have replicate precision within 10 percent or better for most species.
- Radiello samplers were within 20 percent of values from active sampling methods with the following exceptions:
  - Radiello VOC sampler packed with Carbograph 4 is not suitable for collection of 1,3-butadiene. (New cartridge for sampling 1,3-butadiene was not available in time for this project and was not evaluated)
  - Acetaldehyde had poor accuracy probably due to effects from ozonolysis and from low active collection efficiencies.
  - Acrolein could not be accessed due to generally low ambient levels.

HCMS Saturation Monitoring Hypotheses

2. Gradients in pollutant concentrations exist within the Harbor Communities and can be related to a location's proximity to emissions from either stationary or mobile sources. *True for NOx, SO_2, EC, DPM, and less so for BTEX, aldehydes and $PM_{2.5}$.*

3 The long-term air quality monitoring in the area is not adequate to characterize the spatial variations in cumulative exposure within the community. *True with respect to characterizing near-source ambient concentrations, especially near roadways with truck traffic. However, NLB air quality monitoring site is reasonably representative of areas of the community away from traffic.*